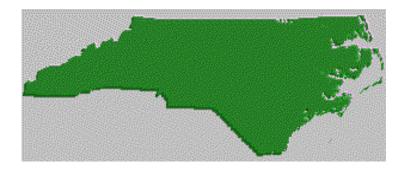
North Carolina

Division of Air Quality

Toxics Protection Branch



Recycled Oil Management Plan

January 2013

Rev. 1: 08/29/01 Rev. 2: 12/9/02

PREFACE

The Plan provides guidance to the processors/refiners of recycled oil to obtain approval from the DAQ to distribute in the State of North Carolina recycled oil that is equivalent "unadulterated fuel". Chemical parameters with recommended analytical methodologies are tabulated in the Plan to establish equivalency to "unadulterated fuel". The Plan provides guidance to the DAQ personnel, recycled oil processors and combustors/burners.

This document also includes details of recycled oil sampling using a variety of sample collection devices from different and varied sources. Details of field activities and sample handling procedures are also included. The samples are generally collected from industrial and/or commercial facilities that have an air quality permit to combust/burn recycled oil.

Terms

DAQ Division of Air Quality

US-EPA United States-Environmental Protection Agency

RCRA Resource Conservation and Recovery Act

PROCESSORS/REFINERS Facilities that carry out chemical and physical operations,

such as blending different quality of recycled oils, filtering out solid contaminants or heating recycled oils to evaporate

water, to produce fuel from the recycled oil and/or to

produce base stock for lubricating oil.

BURNERS Facilities that burn recycled oil for fuel or disposes

recycled oil to generate heat or to power industrial boilers.

BATCH A batch is defined as a specific volume of recycled oil that

has been processed/refined by the processor at its facility to

meet allowable Plan analyte limits (equivalency to "unadulterated fuel") and has a specific batch number

assigned to it.

BATCH SPECIFIC

ANALYTICAL REPORT Analytical report of a above defined batch for the chemical

parameters of the Plan.

CRM/QCS Certified Reference Material/Quality Control Sample

ASTM American Society for Testing and Materials

ICP/MS Inductively Coupled Plasma/Mass Spectrometry

AAS/GRAPHITE FURNACE Atomic Absorption Spectrometry/Graphite Furnace

COLIWASA Composite Liquid Waste Sampler

COC Chain-of-Custody

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Attachments

- Attachment 1 Memorandum of June 11, 1991, Used Oil Burning and Air Permitting Requirements; Memorandum of June 11, 1991, Definition of Unadulterated Fuel; Memorandum of June 11, 1991, Used Oil Analytical Guidelines (No. 2 fuel oil); and Memorandum of July 22, 1991, Used #4 Residual Oil Analytical Guidelines.
- Attachment 2 Drum-Tanker-Rail Car COLIWASA and Drum Thief
- Attachment 3 Recycled Oil Sample Report Form
- Attachment 4 Chain-of-Custody Form
- Attachment 5 ASTM D5495-94, Standard Practice for Sampling With a Composite Liquid Waste Sampler (COLIWASA)
- Attachment 6 Notice of Enforcement Policy
- Attachment 7 Example Form of Recycled Oil Analytical Report and Batch Signature Information
- Attachment 8 North Carolina Approved List of Recycled Oil Suppliers (as of 2/13/2009)
- Attachment 9 Recycled Oil Permitting Procedures
- Attachment 10- On-site Generated Waste (Recycled) Oil Combustion
- Attachment 11- Method 3052: Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices
- Attachment 12- Method 6010B: Inductively Coupled Plasma-Atomic Emission Spectrometry
- Attachment 13- Method 6020: Inductively Coupled Plasma Mass Spectrometry
- Attachment 14- Standard Operating Procedure for Recycled Oil Sample Collection
- Attachment 15- Recycled Oil Sample Aliquoting

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1.0 PLAN OBJECTIVES:

The objective of the plan is to ensure that burners of recycled oil are complying with appropriate regulatory requirements delineated in their air permit. The plan establishes a physical compliance and enforcement mechanism for the Division of Air Quality (DAQ) through specific guidelines for recycled oil sample collection and analyses of relevant chemical parameters.

Included in this plan are details of the approval procedures for recycled oil processors that are planning to distribute their product in North Carolina. The evaluation process involves the determination of whether recycled oil can be deemed equivalent to virgin unadulterated oil.

Implementation of this plan seeks to ensure that all air permit holders using recycled oil that DAQ has approved as equivalent to "Unadulterated Fuel," as defined herein, are meeting relevant requirements. A goal of this plan is also to manage data collection on the quantity of recycled oil burned in North Carolina by facilities holding air permits.

2.0 BACKGROUND:

Recycled oil is defined by US-EPA (1)^a under 40 CFR Part 279 as any oil, that has been refined from crude oil or synthetic oil, which has been used and as a result of such use is contaminated by physical or chemical impurities. *In the text of this plan, all references to recycled and/or used, waste, or self generated oil are intended to carry the same meaning.*

Recycled oil includes oils that are used as hydraulic fluids as well as oils that are used to lubricate automobile engines and other machinery or suspend materials in industrial processes. Oils used for these purposes can be contaminated (2-4) because:

- Engine heat can break down oil additives and other constituents in the oil.
- Dirt, dust and rust can get into the engine crankcase and be transferred into the oil.
- Metal particles from engine wear can also contaminate oil directly.
- Exhaust gases from combustion in the engine can leak through the engine piston rings and into the oil, thus contaminating the oil with gasoline and gasoline combustion products.
- Fluids such as water and antifreeze can leak into the oil during engine operation.

Because of the changes that occur during use, motor oils tend to differ in chemical and physical composition from virgin oil (see Table 1). In general recycled oils have (2):

- Much higher water and sediment levels than virgin oil.
- Relatively higher concentrations of toxic organic compounds.
- Relatively higher levels of metals such as As, Cd, Cr, Pb, etc.

^a Throughout the text, numbers in parenthesis indicate reference numbers.

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TABLE 1. Comparison of Virgin Oil vs Recycled Motor Oil*

Constituent	Virgin Motor Oil (Range, PPM)	Recycled Motor Oil (Range, PPM)
Cadmium	0	0.5 - 3.4
Chromium	0	0.8 - 2.3
Lead	0.03 - 0.28	5.5 – 150

^{*} For details see references 4 and 5.

If managed properly, recycled oil is an valuable resource that can be reused as a base stock for new lubricating oil or as a fuel, since it has a high BTU content. However, if managed improperly, recycled oil can threaten human health and cause damage to the environment.

Federal regulations mandate (6) that used (or recycled) oil must be tested before disposal, and if found hazardous, should be disposed of as hazardous waste under Subtitle C of RCRA (Resource Conservation and Recovery Act). However, if the oil is determined not to be hazardous, it may be disposed of in accordance with RCRA, Subtitle D. In either case, the regulatory requirements are designed to prevent recycled oil from endangering human health and the environment through the disposal process.

Further, US-EPA on September 10, 1992 published (6) its decision not to list recycled oil that is destined for recycling as a hazardous waste. Because Used Oil Management Standards required used oils to be managed in an environmentally safe manner, listing used oil that is to be recycled as a hazardous waste has been considered to be unnecessary by the US-EPA (1). In other words, used oil destined for recycling would be subjected to the Federal Used Oil Management Standards. Waste oil destined for disposal as hazardous waste would be subjected to requirements in RCRA Subtitle C and non-hazardous waste oil would be subjected to requirements in RCRA Subtitle D.

As per US-EPA (6) the key groups involved in this recycling system are:

- **Generators:** Are those who introduce used oil into the used oil management system including automotive generators, industrial generators, do-it-yourself etc.,
- **Transporters:** Are those that transport/carry used oil from generators to those who recycle or otherwise process.
- **Transfer Facilities:** Any transportation related sites, e.g. loading docks or parking lots where shipments of used oil are held for more than 24 hours and less than 35 days.
- Processors/Refiners: Facilities that carry out chemical and physical operations, such as blending different quality of recycled oils, filtering out solid contaminants or heating recycled oil to evaporate water, to produce fuel oil from recycled oil and/or to produce base stock for lubricating oil.
- **Burners:** Facilities that burn recycled oil for fuel or disposes recycled oil to generate heat or to power industrial operations.

 Marketers: Persons/facilities that either determine that used oil meets burning specifications or direct shipments of off-specification recycled oil from their facility to a used oil burner.

Of the above mentioned key groups, only processors/refiners and burners are a focus of this Recycled Oil Management Plan. This focus is mainly because these activities may release increased quantities of toxic chemicals into the environment relative to those from virgin oil, thus causing environmental pollution that may have an increased risk to human health.

3.0 PROGRAM PLAN

3.1 Processor/Refiner:

A processor/refiner is a facility that applies chemical and/or physical treatments to recycled oil to produce fuel oils, lubricants or other recycled oil derived products. Processing includes, but is not limited to, blending recycled oil with virgin oil to meet a required fuel specification, filtration to remove solids and sediments, simple distillation to drive off water and other contaminating volatile compounds, chemical and physical separation and refining. Processors/refiners generally handle large quantities of recycled oil and perform a wide variety of operations and procedures. As a result, these procedures tend to require strict controls (7) because such operations are potentially damaging to the environment and human health.

Federal and North Carolina regulations mandate that recycled oil must be tested to assure that the oil is not a hazardous waste as defined in the Resource Conservation and Recovery Act (RCRA) or polychlorinated biphenyl (PCB) wastes regulated under 40 CFR 761 and incorporated by reference in 15A N.C.A.C. 13A .0118. Under the Recycled Oil Management Plan, recycled oil vendors or processors collect used oil and clean it enough to sell as unadulterated fuel. Under the Plan, the product sold as recycled oil meeting Table 2 parameter limits is approved as essentially equivalent to virgin fuel oil because the vendor/processor typically undertakes various treatment steps. Treatments typically involve batch processing to remove water, filtering and demineralizing to remove solids and additives to produce a batch equivalent to fuel oil. Once treatment is completed for each discrete batch of recycled oil, a representative sample must be collected and analyzed to determine whether key parameters meet Plan limits.

In addition to the stipulations under the Plan, Federal requirements under 40 CFR 761—Polychlorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions—restrict used oil from containing any quantifiable level (defined as 2 ppm) of PCBs. To whom PCB-bearing oil can be marketed and incinerated are further restricted. Under the Federal rules, used oil is presumed to contain quantifiable levels of PCB unless the marketer (vendor/processor) obtains analyses (testing) or other information that refutes this claim. Other information documenting that the used oil fuel does not contain quantifiable levels of PCBs may consist of either personal, special knowledge of the source/ composition of the used oil, or a certification from the generator of the oil claiming that the oil contains no detectable PCBs. Documentation certifying a claim of no quantifiable PCBs and/or other documents relating to

transactions involving PCB-containing used oil must be part of the certification notice(s) supplied to and by each marketer (vendor/processor). Under 40 CFR Part 279, when used oil levels for total halogens are greater than 1,000 ppm, then there is a requirement to test for PCB to meet the 50 ppm PCB limit

For the purposes of this Recycled Oil Management Plan, adherence to the recordkeeping stipulations of the Federal rule serves to document a vendor/processor's claim that their product does not contain detectable PCBs and such documentation must accompany every delivery. An approval for equivalency cannot be granted for used oil containing PCBs as these are absent from virgin oil products.

If valid sample analysis results show that eight key parameters are within the parameter limits of the Plan, and an accompanying certification indicated that the product does not contain detectable PCB's, then the batch is considered to be equivalent to virgin oil. The eight key parameters subject to Plan limits are:

Eight key parameters	Parameter Limits
1. Arsenic	1.0 ppm weight basis
2. Cadmium	2.0 ppm weight basis
3. Chromium	5.0 ppm weight basis
4. Lead	100 ppm weight basis
5. Total halogens	1,000 ppm weight basis
6. Sulfur *	a. 0.50 % weight basis for No. 2 fuel oil
	b. 2.0 % weight basis for No. 4, 5, or 6 fuel oils
7. Ash	1.0 %, weight basis
8. Minimum flash point *	a. 100 °F for No. 2 fuel oil
	b. 130 °F for No. 4 fuel oil
	c. 175 °F for No. 5 or 6 fuel oils

^{*} Note: Parameter limits differ for various fuel grades of No. 2, 4, 5, and 6 fuel oils. ppm = parts per million

3.1.1 Initial Approval Requirements for Processors/Refiners:

In North Carolina, processors/refiners must request, in writing, for approval from the DAQ that their refined/recycled oil be considered equivalent to virgin oil as defined in the memorandum "Definition of Unadulterated Fuel" of June 11, 1991 (see Attachment 1 for definition) and "Used Oil Analytical Guidelines" as specified in Table 2. Such an approval request must be supported by submitting analytical results from at least three different batches of recycled oil which addresses all chemical parameters included in Table 2, "Recycled Oil Analytical Guidelines." The analytical reports will be reviewed and evaluated for compliance with the parameters in Table 2. The Section Chief, Technical Services Section, DAQ, will issue final approval, for equivalence to virgin oil.

For approval, a vendor/processor must specify the recycled fuel oil equivalency number, *i.e.* No. 2, 4, 5, or 6 fuel oils, for which a vendor/processor plans to sell as approved recycled oil in North Carolina. A written statement by the vendor/processor requesting approval for equivalency is necessary and must accompany the analytical results from 3 separate batches (establishing equivalency to virgin oil) for each recycled fuel oil number. Equivalency determination is available for No. 2, 4, 5, or 6 fuel oils, but must be individually demonstrated for each fuel oil number for which a vendor/processor plans to sell approved recycled oil in North Carolina. Equivalency must be demonstrated for each discrete recycled fuel oil number (*i.e.*, No. 2, 4, 5, and 6). In other words, approval for one particular fuel oil number does not extend to any other fuel oil without demonstration to and approval by DAQ.

As part of the initial approval process, processors will also be required to analyze recycled oil Certified Reference Material (CRM)/Quality Control Samples (QCS) provided by the DAQ. Such samples or combinations thereof, will be purchased by DAQ from a vendor who shall certify the analyte concentrations. Results from the analysis of such CRM/QCS samples along with analytical results of three different batches of recycled oil samples of the processor will be considered by the Section Chief for granting approval to distribute recycled oil in the State of North Carolina.

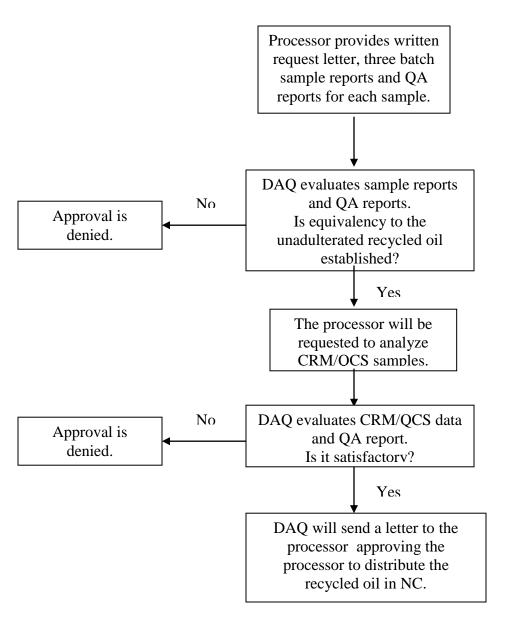
The following steps summarizes the initial processor approval process:

- 1. The processor requests approval to become an approved recycled oil supplier via written request. This request includes analytical results of three different batches of recycled oil.
- 2. DAQ evaluates analytical results and the laboratory's QA performance (see section 3.4 Note 4) of three batches for equivalency to the unadulterated recycled oil.
- 3. If DAQ is unable to establish equivalency via data evaluation process, then approval is denied.
- 4. If DAQ is able to establish equivalency, then the processor will be requested to analyze CRM/QCS samples.
- 5. DAQ evaluates CRM/QCS data and if the analytical performance QA report is unsatisfactory, approval is denied.
- 6. If the analytical results and the laboratory's QA performance are satisfactory, then DAQ will send an approval letter to the processor to distribute the recycled oil in the State of North Carolina.

Figure 1 is an initial processor approval process flowchart.

Figure 1

Initial Processor Approval Process Flowchart



3.1.2 Operating Requirements for An Approved Vendor/Processor

Approved vendors/processors must document and maintain organized records for a period of three years for each of the following four key items: Facility-specific (1) tank batch volume(s); (2) Batch analysis results; (3) Batch signature information; and (4) Delivery manifest. Failure to perform and document fulfillment of the key operating requirements will jeopardize a vendor/processors approval status. The following discussion describes and defines the key operating requirements and how they are to be managed.

1. Tank batch volume(s)

The recycled oil vendor/processor must certify and document the volume of each tank containing a completely treated batch¹ of recycled oil. Tank manufacturer information specifying the tank size in gallons will be considered in determining the batch volume of each tank. A recycled oil vendor/processor may have more than one tank at a facility to contain a completely treated batch of recycled oil. If multiple tanks containing completely treated recycled oil are used, the vendor/processor must establish batch volumes for each separate tank. In addition, the vendor/processor must determine and document the batch frequency.²

2. Batch analysis results

The recycled oil vendor/processor must collect a representative sample of each batch and analyze each batch sample for the eight key parameters using the analytical methods in Table 2. The recycled oil vendor/processor must receive the batch analysis results and ensure the eight key parameters meet the Table 2 Plan limits before shipping any of the batch. The recycled oil vendor/processor must document and record representative sample analysis results³ for each batch relative to the Plan limits for the eight key parameters on the delivery manifest showing that the eight key parameters meet the Plan limits. The analytical report from the vendor/processor shall be in a similar format as in Table 2 of the Plan, meaning the report shows the analysis results along with the limits. Note: once a "batch" has been analyses no additional material can be added in unless re-analysis occurs. And the oil cannot be sold or distributed until satisfactory analyses are obtained and documented.

3. Batch signature information

The recycled oil vendor/processor must document and record batch signature information uniquely identifying, and characterizing the eight key parameters in, each individual batch that

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¹ The term 'batch' is defined as a facility-specific volume of recycled oil that has been processed/treated by the vendor/processor to meet the Plan limits (i.e., equivalency to "unadulterated fuel" in terms of the eight key parameters). It is the size (in gallons) of the holding/storage tank containing the treated recycled oil from which a representative sample is collected for analysis

² The term 'batch frequency' is defined as the amount of time to process one (1) batch volume

³The term 'batch analysis results' is defined to be the results for the eight key parameters using the corresponding appropriate sample preparation and analytical methods in Table 2 taken from a representative sample of a batch.

has undergone complete treatment. The batch signature information to accompany delivery consists of:

- a. Batch number,
- b. Tank identification with batch volume of recycled oil,
- c. Date and time the batch completed treatment, and
- d. Volume(s) delivered to the burner facility.

4. Delivery manifest

The delivery manifest for recycled oil is the document clearly showing the shipment content and amount, its place and date of loading and place and date of destination, as is customary in the delivery industry. The delivery manifest from the vendor/processor to the burner shall accompany the delivery shipment and include the batch signature information and batch analysis results. The certification indicating that the used oil does not contain detectable (2 ppm) PCBs shall also accompany the delivery manifest.

To set a reasonable time limit on the validity of batch analysis results, submitted analytical results of the samples representative of the recycled oil shipment from the vendor/processor to the burner shall be no more than one year old. This in effect limits the acceptable age of a batch to no more than one year old without a repeat analysis documenting acceptability and assurance.

3.1.3 Requirements for Re-Approval of Vendor/Processors

After initial approval, the processor shall be re-approved every five (5) years. The re-approval process is similar to the initial processor approval process involves the following:

- 1. The processor sends analytical results of three different batches of recycled oil.
- 2. Repeat the initial process 2 6.

Approximately once a year, all approved processors may also be required to analyze recycled oil CRM/QCS submitted by DAQ to assure continual data quality. The processor's continued approval shall be dependent on the satisfactory performance of the CRM/QCS samples. A $\pm 20\%$ deviation from the true value of the CRM/QCS samples for analyses of the Plan will be considered as a processor's satisfactory performance.

A list of the currently approved recycled oil processors is included as Attachment No. 8 (no particular processor is recommended by DAQ).

The DAQ may find, through its own testing and analysis, that a specific supplier consistently fails to comply with the parameter limits allowed for meeting the equivalency to unadulterated virgin oil. Consequently, the supplier would be notified that he has no longer managed to maintain his equivalency approval and consequently it will affect his approval status.

TABLE 2. Recycled Oil Parameter Limits¹ and Analytical Guidelines ²

Parameter	Parameter Limit ¹	Analytical Method ³	Detection Limit (DL) ⁴
Arsenic (ppmw)	1.0	EPA SW- 846 3052 and 6020	0.10
Cadmium (ppmw)	2.0	EPA SW- 846 3052 and 6020	1.0
Chromium (ppmw)	5.0	EPA SW- 846 3052 and 6010B	1.0
Lead (ppmw)	100	EPA SW- 846 3052 and 6020	1.0
Total Halogens (ppmw)	1000	EPA SW- 846 9076	100
Sulfur No. 2 oil (% by weight)	0.50	ASTM D4294	0.05
Sulfur No. 4, 5, or 6 oil (% by weight)	2.0	ASTM D4294	0.05
Ash (% by weight)	1.0	ASTM D482-95	0.05
Flash Point Minimum No. 2 oil (°F)	100	ASTM D56-96	NA
Flash Point Minimum No. 4 oil (°F)	130	ASTM D-93	NA
Flash Point Minimum No. 5, 6 oil (°F)	175	ASTM D-93	NA
BTU/lb. Or BTU/gal.	NR	ASTM E771-90	0.05
Sp. Gravity, lb./gal.	NR	ASTM D287-92	0.05
Moisture %	NR	ASTM D95-83	0.05
Viscosity, SUS ⁴	NR	ASTM D445-96	0.05

^{1 =} Maximum limits as per North Carolina Air Toxics regulations, except where specified as minimum limits. Limits on Parameter 1 – 7 are on a weight basis.

^{2 =} See subsection 3.4 for additional details under Note 1.

^{3 =} Specified analytical method. (See Section 3.4)

^{4 =} The minimum concentration of the analyte that can be measured with 95% confidence.

NA = Detection limit not available.

ppmw = Parts per million by weight for arsenic, cadmium, chromium, lead, and total halogen

3.2 Requirements for Burners:

Burners combust recycled oil as a fuel to generate steam/heat for industrial operations. Such facilities are required to obtain an air permit from the DAQ in order to legally operate their combustion source in North Carolina (see Attachment 1, Air Permitting Requirements memorandum dated June 11, 1991 and Attachment 9, Recycled Oil Permitting Procedures, draft dated August 27, 1999). The combustion source is <u>not</u> required to obtain an air permit to burn on-site generated recycled (waste) oil <u>provided not more than 500 gallons are burned in any single calendar year (see Attachment 10).</u>

Facilities/sources burning recycled oil shall not accept any recycled oil without a batch specific analytical report showing the oil to be within the parameter limits specified in Table 2 and that a certification that the used oil does not contain detectable (2 ppm) PCBs accompanies the analytical report. The delivery manifest from the vendor/processor shall also include batch signature information, which consists of:

- 1. Batch number,
- 2. Tank identification with batch volume of recycled oil,
- 3. Date and time the batch completed treatment, and
- 4. Volume(s) delivered to the burner facility.

It shall be the recycled oil vendor/processor's responsibility to deliver a manifest, PCB certification and an analytical report of the batch delivered to the burner's facility. Attachment 7 of the Plan presents an example form containing all the stipulated information for a manifest and an analytical report on a single page.

It shall be the recycled oil processor's responsibility to deliver a manifest and an analytical report along with the batch delivery to the burner's facility.

When an oil sample is identified as not meeting the equivalency criteria as specified in your air quality permit, a NOTICE of VIOLATION will be issued to the facility combusting the oil even if the approved supplier has provided you an analysis, which indicates that the recycled oil shipment was in compliance with the unadulterated oil specifications (see Attachment 6).

The DAQ shall include a stipulation in the air permits of those facilities combusting recycled oil that will require each facility to report to their respective Regional Office, within 30 days after the end of each calendar year, the total gallons of recycled oil combusted at the facility for the previous twelve (12) months (calendar year). Each Air Quality Regional Office will send copies of all annual reports to the Toxics Protection Branch. These data may be used by to calculate the total annual consumption of recycled oil in North Carolina.

A copy of the "Recycled Oil Permitting Procedures" is included as Attachment No. 9.

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3.3 Definition of Unadulterated Fuel:

In Attachment 1, the DAQ memorandum of June 11, 1991 defines "unadulterated fuel" as "fuel oils, coal, natural gas, liquefied petroleum gas, and wood to which no toxic additives have been added. The term toxic additives refers to additives or contaminants which could result in the emission of toxic air pollutants of the North Carolina air toxics regulation."

These air toxics regulations are listed in 15A NCAC 2D.1100, Control of Toxic Air Pollutants and 15A NCAC 2Q .0700, Permit Requirements for Toxic Air Pollutants.

"Used oil is considered equivalent to unadulterated fossil fuel if toxics are demonstrated to be at a level of no greater concern than those of unadulterated fuels. The permit applicant, or supplier of the used oil, must demonstrate to the satisfaction of the DAQ Director that the used oil toxic additives or contaminants are at a level such that it could be defined as unadulterated."

3.4 Recycled Oil Analytical Guidelines:

Representative sample(s) of recycled oil must be collected as per the sampling procedure outlined below in Sections 4, 5 and 6 and analyzed for the chemical parameters included in Table 2.

Note 1.

US-EPA SW 3052 and 6020 are the methods being specified by this Plan for recycled oil sample analyses for arsenic, cadmium and lead. US-EPA SW 3052 and 6010B is the specified method for chromium. Empirical work indicates that recycled oil samples must be sufficiently digested/prepared before aspiration into the ICP/MS or an AAS graphite furnace. Further empirical evidence derived from work with reference material oil indicate that the EPA method 3052 (see Attachment 11) does the most efficient job of destroying organic material contained in the sample matrices, providing a clear-colored solution. The clarity of the digested solution is an indication of the degree to which organic material in a recycled oil sample has been destroyed. If this material is not disengaged from the sample matrix, it may interfere during the analysis process possibly producing biased results.

A different analytical technique for chromium is necessary because empirical data suggests a positive bias due to carbon interference under ICP/MS analysis. This bias is significantly eliminated under ICP/AES analysis. ICP is preferred because of its multi-element capabilities. Analytical sensitivity, specificity and reliability of As and Cd in recycled oil samples have been determined to be improved with ICP/MS (see Attachment 12, 13).

Note 2:

Processors should note that the requirements, particularly for arsenic and total halogens for recycled oil to be distributed as a fuel for combustion in North Carolina differ somewhat from Federal requirements given in 40 CFR Part 279 and may also differ from requirements in other states. For arsenic, the limit is set at 1.0 PPM and for total halogens 1000 PPM. Therefore, recycled oils containing > 1.0 PPM of arsenic and/or > 1000 PPM of total halogens are considered to be <u>not</u> equivalent to "unadulterated fuel". Such fuel type will not be burnt in the

DAQ permitted boilers in the State of North Carolina and must be disposed of accordingly.

Note 3:

In case a recycled oil sample is analyzed multiple times by the DAQ and/or the processor. The reported analytical result shall represent an arithmetic <u>mean</u> of all analyses with a calculated Percent Relative Standard Deviation (%RSD) from the reported mean value. The percent RSD will be calculated by dividing the standard deviation by the mean of multiple analyses and multiplying the resultant by 100.

Note 4:

Laboratory Quality Assurance Report

Each analysis report from laboratory should include a quality assurance report. Quality assurance report should contain the following information:

- Analysis parameter
- Test method
- Reporting limit
- Percent recovery for lab control sample
- Percent recovery for matrix spike
- Results for method blank
- Replicate analysis results

For metals analysis (Arsenic, Cadmium, Chromium and Lead) the acceptable recovery range for laboratory control sample is 85%-115%.

Acceptable range for matrix spike samples is 75% - 125%.

For all other analysis parameters the acceptable recover range for laboratory control sample is 90% - 110%. Acceptable range for matrix spike samples is 80% - 120%.

Table 3 shows laboratory's QA performance and criteria.

TABLE 3. Laboratory Quality Assurance

Analysis Parameter	Test Method	Reporting Limit	% Recovery for lab control sample	% Recovery for matrix spike
Arsenic	EPA SW- 846 3052 and 6020	0.10	85% - 115%	75% - 125%
Cadmium	EPA SW- 846 3052 and 6020	1.0	85% - 115%	75% - 125%
Chromium	EPA SW- 846	1.0	85%- 115%	75% - 125%
	3052 and 6010B			
Lead	EPA SW- 846	1.0	85%- 115%	75% - 125%
	3052 and 6020			
Total Halogens	EPA SW- 846 9076	100	90%- 110%	80% - 120%
Sulfur No.2, 4,5,6	ASTM D4294	0.05	90%- 110%	80% - 120%
Ash	ASTM D482-95	0.05	90%- 110%	80% - 120%
Flash Point	ASTM D-93	NA	90%- 110%	80% - 120%
Minimum No.2,4,5,6				
BTU	ASTM E771-90	0.05	90%- 110%	80% - 120%
Sp. Gravity	ASTM D287-92	0.05	90%- 110%	80% - 120%
Moisture	ASTM D95-83	0.05	90%- 110%	80% - 120%
Viscosity	ASTM D445-96	0.05	90%- 110%	80% - 120%

4.0 SAMPLING OF RECYCLED OIL

The purpose of manual sample collection is to obtain a small amount (~1000 ml) of recycled oil from a selected oil receptacle or container (tank, drum, barrel, boiler, etc.) that is considered to be representative of the recycled oil being burned. A representative sample is defined as a small portion of recycled oil collected from the total volume that contains the same chemical constituents and in the same proportions that are present in the total volume. It is essential that a representative sample of oil be collected to obtain accurate chemical data about the quality of oil in any particular container. Such data can justifiably be used for compliance and enforcement purposes.

Activities related to representative sample collection of recycled oil are summarized in Table 4 and are discussed briefly below.

TABLE 4

Summary of Activities Relat	ed to Recycled Oil Collection
Sample Activity	Program Plan
Equipment	Polyethylene Composite Liquid Waste Sampler (COLIWASA) and/or Drum Thief
Container	New 1000 ml Brown Nalgene™ Bottle
Volume	950 ml
Labeling and Identification	Use self-adhesive label and give sample number in the field and write details in the "Recycled Oil Sample Report."
Storage and Transportation	Samples are stored and shipped in closed containers. Transport samples to Toxics Lab within 3 working days. At the Toxics Lab, samples are aliquoted within 5 working days and sent to analytical labs.

4.1 Safety

It is DAQ policy that personnel safety is of ultimate importance. In many cases, DAQ personnel must determine in the field whether or not sampling can be conducted in a controlled and safe environment. If DAQ personnel consider the situation unsafe, the first priority is to leave the scene. Otherwise all safety precautions should be taken while collecting recycled oil samples. For most sampling inspections, Level D type protective clothing is appropriate. This generally includes the use of steel-toed safety shoes or boots, hardhat, and safety glasses. Facility personnel should collect the sample, while a DAQ inspector is there to observe the collection process and to make sure that DAQ sample collection procedures are followed. Always take a waste container for disposal of wipes and gloves and dispose of these items in an appropriate waste container on the facility property.

4.2 Arrival at the Facility

Upon arrival at a facility to collect a recycled oil sample, DAQ personnel should inform the facility owner/operator that a duplicate sample will be offered to them in a State-provided container. The owner/operator should also be informed that, upon completion of the sampling,

he/she will be asked to sign the sample report form acknowledging acceptance or rejection of a duplicate sample.

The purpose of collecting duplicate samples is to allow the facility the opportunity to analyze the "same" substance the State will analyze. When gathering field equipment and sample containers prior to the sampling event, sampling personnel should bring enough containers to provide the facility with duplicate samples. If recycled oil sampling is a part of a facility-wide inspection, it is recommended that recycled oil samples be taken at the end of an inspection so that Chain-of-Custody can be easily maintained.

Further, obtain a copy of the analytical report of the recycled oil batch that you will be sampling and attach it to the "Recycled Oil Sample Report". The facility should have a copy of this report readily available, if not, make arrangements for the TPB to receive this report later.

4.3 Sampling Equipment

Depending on the container, collection of recycled oil may require special sampling devices. All sampling devices and equipment are disposable and should never be reused. Consequently, there are no cleaning methods recommended prior to sampling.

For this program, barrels, drums, tanks and tank cars may be sampled using a disposable polyethylene COLIWASA (Composite Liquid Waste Sampler) and for small cans a Drum Thief sampler is recommended (see description in Attachment 2 and additional details in 5.2 and 5.3 below).

4.4 Sample Container

Sample containers come in a variety of sizes, shapes and materials. When selecting the proper container for a given application, one must have knowledge of the materials to be sampled to ensure there is no interaction between the sampled material and the container, as this would affect the sample integrity. A 1000 ml brown NalgeneTM bottle is recommended for all sampling to protect potential light-sensitive materials. USE ONLY NEW BROWN NALGENETM BOTTLES. Used bottles should be discarded to prevent possible cross-contamination. Do not fill to more than 95% of the bottle capacity. This will leave room for thermal expansion of the sample during storage and transport.

4.5 Sample Volume

Analytical requirements essentially dictate the sample volume. However, it is always better to have more sample than what is required for analyses. A 950 ml sample (95% capacity of a 1000 ml brown NalgeneTM bottle) is recommended.

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4.6 Sample Labeling and Identification

It is imperative that the sample collected be immediately capped, labeled and adequately identified. All samples are to be labeled immediately after collection in the field. Each Nalgene™ bottle will be labeled using a "self-adhesive label" and should be additionally secured using clear tape to prevent accidental defacing of the label. The person collecting the sample should record the sample number on the label using the following format: (example: Region/Date (month, day, year)/Sample Number - "WSRO/031798/01" − Winston-Salem Region/March 17, 1998/sample 01). Inspectors collecting samples in the same region, on the same day, should take precautions to prevent duplication of sample numbers. Therefore, inspectors should put their initials on the label, in case two samples are accidentally sent to the laboratory with the same number. This way it may be possible to differentiate between samples to know who should be contacted. The date in the sample number should always include two digits for each part (month-03, day-17, year-01).

Use the following letter designations for your respective region when assigning sample numbers:

ARO Asheville Region = FRO Fayetteville Region = Mooresville Region **MRO** Raleigh Region RRO Washington Region WARO Wilmington Region WIRO =WSRO Winston-Salem Region = Raleigh Central Office **RCO** =

The "Recycled Oil Sample Report" (see Attachment 3) is an important document to be completed by DAQ personnel during each sampling event. Incomplete Recycled Oil Sample Report forms will be returned for corrections by the regional DAQ inspector who collected the sample. At a minimum this report shall include the following:

- a. Sample number (as described above)
- b. Date and time the sample was collected
- c. Facility ID number (County/Prem number)
- d. Name of facility sampled
- e. Description of sample point (boiler feed line, tank, drum, etc.)
- f. Recycled oil supplier information
- g. Parameters for analysis
- h. Type of recycled oil sampled (#2, #4, etc.)
- i. Duplicate Sample Taken Yes or No (signed)
- j. Remarks Describe any difficulty in sample collection, sample condition, weather problems, etc.
- k. Name of the person collecting sample(s)
- 1. Signature of sample collector

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If samples are collected from more than one facility the same day, a separate "Recycled Oil Sample Report" for each facility shall be completed and the sample number will increase sequentially.

A copy of the "Recycled Oil Sample Report" shall be shipped along with all samples to the Toxics Protection Branch Laboratory (see 4.7 below for the mailing address).

The "Recycled Oil Sample Report" should be accompanied with the "Chain-of-Custody" form (see Attachment 4).

4.7 Sample Storage and Transportation

After collection, each recycled oil sample should be closed (capped) to minimize moisture and dust contamination, effects of sun light and prevent loss of volatile organic constituents.

All samples should be sealed with a Chain-of-Custody (COC) seal and placed in the shipping container (Pelican Case) along with a completed Recycled Oil Sample Report form and a Chain-of-Custody form. This will ensure that chain-of-custody is maintained for each sample being shipped.

Recycled oil samples should be shipped by Courier Mail on pre-printed labels to:

Toxics Protection Branch Laboratory Division of Air Quality 1622 Mail Service Center Raleigh, NC 27699-1622

COURIER #52-01-00

All recycled oil samples should be shipped within THREE workdays after collection. After arrival at the laboratory, each sample will be aliquoted within FIVE working days and forwarded to an appropriate analytical laboratory for analysis.

5.0 RECYCLED OIL SAMPLE COLLECTION PROGRAM

The recycled oil sampling program may require that samples be collected from a variety of different sources and occasionally from difficult-to-reach sampling points. Therefore, details of each and every situation cannot be included in this document, however, examples of the more common sampling points are outlined below.

It is anticipated that most recycled oil samples will be collected from facilities burning recycled oil in boilers, kilns, rotary dryers or furnaces. Such facilities may have recycled oil contained in tanks, tank cars, barrels, drums, cans, etc. Consequently, sampling procedures detailed below address these types of sources. However, upon request to the Toxocs Protection Branch,

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technical details related to any other special point sources can be obtained. The procedures included here are those that are approved and recommended by the American Society for Testing and Materials (ASTM) {see Attachment 5, ASTM D5495-94 enclosed for additional details}.

The following sample procedures outlined here probably represent the majority of the sampling situations that may be encountered.

5.1 Manual Burner Feedline Sampling

Feedline sampling is the preferred method since compositionally it represents the actual oil being combusted at the time of the sample collection. Most burner fuel feed lines have a sample tap in the line from which an oil sample can be collected. If the fuel feed line does not have a sample tap, ask the facility personnel to have one installed for future sampling events. When sampling from a burner fuel feed line, flush the sample tap and line until they are adequately (at minimum two volumes of the sample tap) purged. Collect the sample into a 1000 ml brown Nalgene™ bottle, cap, label and transport to the laboratory for chemical analysis of desired parameters as listed in Table 2 (See Attachment 14 " Standard Operating Procedure for Recycled Oil Sample Collection").

Caution: The fuel in these feed lines will be under pressure and may also be heated. Therefore, take extreme care when opening the valve for sample collection.

5.2 Storage Tanks and Tank Cars

If it is not possible to collect a recycled oil sample from the fuel feed line, then it will be necessary to collect the sample from an alternate location such as a storage tank or tank car. Storage tanks and tank cars generally hold large volumes. These storage vessels should be sampled by inserting an open disposable polyethylene COLIWASA, 7/8 inch diameter and 7 feet long, into the top of the tank to a depth of approximately six inches to one foot from the bottom This will help in avoiding the collection of water that may have settled to the bottom. Pull the plunger on the COLIWASA to seal the end while removing the sample. Release the sample into a sample bottle and repeat this process until the desired sample volume (950 ml) is reached.

Remember personal safety precautions should be exercised when collecting samples from tanks or tank cars. Climbing to the top of a tank or tank car to collect samples can be risky, as one can slip and fall. The facility should provide adequate personal protection for the safe collection of recycled oil samples. A platform or man lift with safety handrails is the minimum safe work area that should be used by the facility personnel during the sampling process. Details of such sampling and/or sample locations should be described in the "Recycled Oil Sample Report" under the sample point description. Additional disposable polyethylene COLIWASA samplers, 7/8 inch diameter and 7 feet long, are commercially available for tank and tank car sampling.

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5.3 Drums, Barrels and Cans

Occasionally, recycled oil may be stored in drums, barrels or small cans that may need to be sampled. Therefore, when sampling these containers, withdraw a sample from the center of the barrel/drum/can using the sampling procedure described below.

Barrels, drums and cans containing recycled oil can be sampled using a disposable polyethylene COLIWASA or drum thief. For drums and barrels, a 7/8" diameter and 42" long COLIWASA made of polyethylene is ideal. The COLIWASA can hold up to 250 ml of sample volume and operates the same as described in section 5.2 above. For sample collection, insert the COLIWASA in a drum/barrel and collect a sample. Take the COLIWASA out of a drum/barrel and transfer the sample into a 1000 ml brown sample NalgeneTM bottle. Additionally, a Drum Thief (12-mm in diameter and 42 inches long) may be used instead of the COLIWASA. To collect a sample, insert the Drum Thief into the container, cover the open end with your thumb, remove the device and transfer the sample into a 1000 ml brown NalgeneTM bottle. Continue this process until the desired sample volume is achieved.

6.0 RECYCLED OIL SAMPLE ANALYSES PROGRAM

Table 5 summarizes the chemical parameters and the laboratories that will receive and analyze recycled oil samples.

TABLE 5

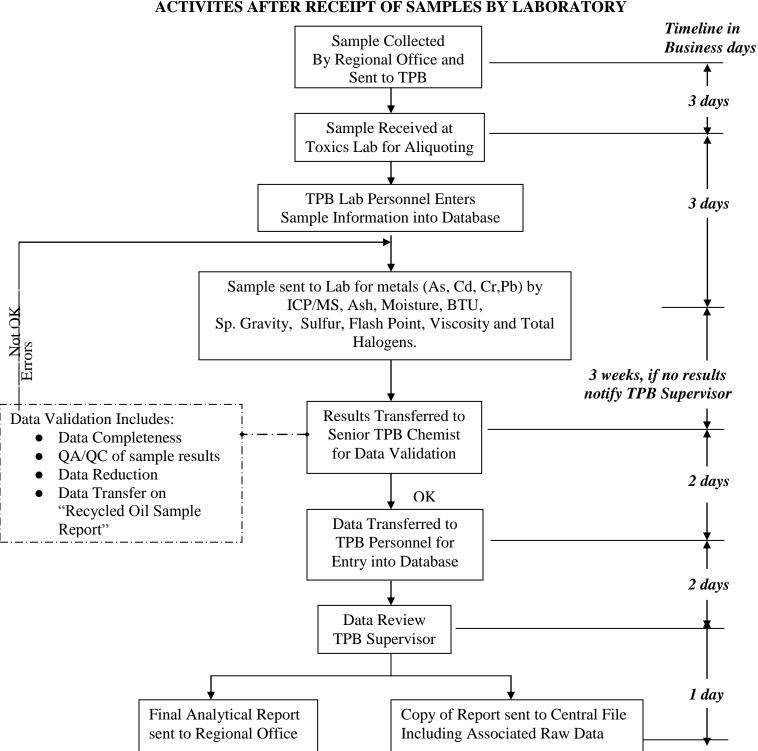
Recycled Oil Sample Analysis Plan		
Laboratory	Chemical Parameter*	
Contract Lab	Metals by ICP/MS (As, Cd, Cr, Pb), BTU, Sp. Gravity, Ash, Moisture, Total Halogens Sulfur, Flash Point and Viscosity	

^{*} For details of analysis methods, refer to Table 2.

Included in Figure 2 are details of activities after receipt of recycled oil samples at the Toxics lab for chemical analysis. Additionally, an example copy of the "Recycled Oil Analytical Report and Batch Signature Information" report is included as Attachment 7 (See attachment 15 "Recycled Oil Sample Aliquoting").

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Figure 2
ACTIVITES AFTER RECEIPT OF SAMPLES BY LABORATORY



REFERENCES

- 1. U.S. Environmental Protection Agency, Hazardous Waste Management Systems; Identification and Listing of Hazardous Waste; Recycled Used Oil Management Standards., Fed. Reg. 57 (176): 41566-41626., Sept. 10, 1992.
- 2. Mueller Associates, Waste Oil: Reclaiming Technology Utilization and Disposal., Park Ridge, N.J. Noyes Data Corporation, 1989.
- 3. Byrne, J.P., C.A. Cody, P.J. Doyle, J.S. MacKinnon, A. A. Mayor, A.M. Reid, S.K Rosner, and C. J. Talbot., Used Motor Oil in Massachusetts: A Prioritization of End Uses Based on Human Health and Environmental Risk. Prepared for the Commonwealth of Massachusetts-Department of Environmental Protection by Tufts University-Department of Civil Engineering, 1989.
- 4. U.S. Environmental Protection Agency., Composition and Management of Used Oil Generated in the United States., EPA/530-SW-013, Washington, D.C. 1984.
- 5. U.S. Environmental Protection Agency., Hazardous Waste Management System: General Identification and Listing of Hazardous Wastes: Used Oil., Fed. Reg. 56 (184): 48000-48074., Sept. 23, 1991.
- 6. U.S. Environmental Protection Agency., Environmental Regulations and Technology-Managing Used Motor Oil, EPA/625/R-94/010, Page 3, Dec. 1994.
- 7. U.S. Environmental Protection Agency., Environmental Fact Sheets: Management Standards Issued to Control Potential Risks from Recycled Used Oil-No Hazardous Waste Listing., EPA/530-F-92-018, Washington, D.C. 1992.

ATTACHMENTS

Attachment 1 is provided for historical context, even though some statements are no longer valid because new rules or policies have superceded them, including:

- June 11, 1991 Memorandum on Used Oil Burning Air Permitting Requirements
- A. Page 1, last sentence of 1st paragraph. "This process also requires an air toxics review" is no longer valid. Given that recycled oil is considered and demonstrated to be equivalent to unadulterated fuel oil, burning recycled oil causes no additional toxic or hazardous emissions, and accordingly requires no additional regulatory requirements.
- B. Page 2, Reference to 15 NCAC 2H .0610 (a)(2) in Policy Item 1 and 2 is no longer valid, given that 15 NCAC 2H .0610 was repealed in April 1999.
- June 11, 1991 Memorandum on Used Oil Analytical Guidelinesir Permitting Requirements

In 1991 only No. 2 equivalent recycled oil was available and the corresponding allowable levels for flash point and sulfur content were accordingly set specific for No. 2 fuel oil. Since then, recycled oil is now available in No. 4, 5, and 6 equivalent forms, and Table 2 of the Plan sets specific allowable levels for recycled oil:

- Flash point for No. 2 at 100 °F, No. 4 at 130 °F, and Nos. 5 and 6 at 175 °F;
- Sulfur content for No. 2 at 0.50%, and for Nos. 4, 5, & 6 at 2.0 %.



Air Quality Section June 11, 1991

MEMORAHDUM

TO:

Regional Supervisors

Regional Air Quality Engineers

Assistant Chiefs Earl
Air Permits Branch Staff

FROM:

George T. Everett, Director

Division of Environmental Management

SUBJECT:

Used Of 1 Burning

Air Permitting Requirements

Background

 The Air Quality Section recognizes that burning used oil has become a popular way to deal with used oil collected at numerous sites throughout the State. Air permitting rules currently require sources desiring to burn used oil to obtain an air quality permit. This process also requires an air toxics review.

Because such permit reviews are usually handled at headquarters, a significant time lag occurs between the time of permit application submittal and permit issuance. This has resulted in a critical situation for collectors/recyclers of used oil who have had to slow down or halt used oil collections because their clients cannot get permitted to burn used oil quickly enough. In addition, the lack of collection of used oil in North Carolina will have a negative impact on the environment.

Therefore the Air Quality Section has developed the following policy to address this issue so that permits can be issued more quickly to applicants desiring to burn used oil. In developing this policy, the Air Quality Section recognizes that used oil is a typical additive to "normal" fuel oil.

Please refer to the attached memoranda. I have determined that used oil
meeting the following criteria is equivalent to unadulterated fossil fuel
for the purposes of the North Carolina air toxic regulation.

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- a. "Definition of Unadulterated Fuel" of June 11, 1991; and
- b. "Used Oil Analytical Guidelines" of June 11, 1991.

Memo Page 2 June 11, 1991

Palicy Part

- For UNPERMITTED NEW SOURCES, although an air permit is required, the Air Quality Section will not require an air toxic review for the burning of used oil for combustion sources subject to 15A NCAC 2H .0610(a)(2), provided the air permit applicant has:
 - a. submitted an air permit application; and
 - b. demonstrated that the used oil toxic additives and contaminants have been reduced to a level such that the used oil is equivalent to unadulterated fossil fuel. This demonstration can be made with information from the used oil supplier.
- 2. For EXISTING PERMITTED SOURCES that are already permitted to burn an unadulterated fuel oil, subject to 15A NCAC 2H .0610(a)(2), but would like to burn an approved used oil, the Air Quality Section can exempt these sources from an air toxic review for the burning of used oil, and the source can begin or continue to burn used oil, provided that within one hundred and twenty (120) days from the date of this memorandum:
 - a. the applicant has notified the appropriate Regional Office in writing of its intent to burn a <u>specific</u> approved used oil. The Regional Office will revise the applicant's existing air permit. These permit revisions are considered to be technical changes and therefore a permit fee will be required.
 - b. the permit applicant has demonstrated that the used oil toxic additives and contaminants have been reduced to a level such that the used oil is equivalent to unadulterated fossil fuel. This demonstration can be made with information from the used oil supplier.
- 3. Neither new nor existing permitted sources are exempt from Prevention of Significant Deterioration (PSD) review requirements. For asphalt plants that are major PSD sources, throughput of approximately 409,276 gallons per year would trigger PSD review requirements for a modification for particulates (before applying control efficiency). A throughput of approximately 563,000 gallons per year would trigger PSD review requirements for a modification for sulfur dioxide (before applying control efficiency for sources with scrubbers).
- 4. The air permit shall be conditioned so as to require the permit applicant to provide to the appropriate Regional Office on an annual basis, the total throughput of the used oil and the results of analytical testing of the used oil.

Attachments

cc: Lee A. Daniel Laura S. Butler Earl McCune Sandra Birckhead

Air Quality Section June 11, 1991

MEMORANDUM

TO:

Sammy Amerson

On For RH

FROM:

Russell Hageman

SUBJECT: Definition of Unadulterated Fuel

Unadulterated fossil fuel means fuel oils, coal, natural gas, liquefied patroleum gas, and wood to which no toxic additives have been added. The term toxic additives refers to additives or contaminants which could result in the emission of toxic air pollutants of the North Carolina air toxics regulation.

Used oil is considered equivalent to unadulterated fossil fuel if the toxics are demonstrated to be at a level of no greater concern than those of unadulterated fuels. The permit applicant or supplier of the used oil must demonstrate to the satisfaction of the Director that the used oil toxic additives or contaminants are at a level such that it could be defined as unadulterated.

Please refer to the attached memorandum "Used Oil Analytical Guidelines" dated June 11, 1991.

Attachment

cc: Leu Daniel

Laura Butler Earl McCune Sandra Birckhead

Thomas Allen

Regional Air Supervisors

AIR QUALITY SECTION

MEMORANDUM

June 11, 1991

To:

Lee Daniel

From:

Earl McCune SHIN

Subject: Used Oil Analytical Guidelines -

Based on a study of emission factors from #2 fuel oil, used oil, and analyses of used oil from Noble Oil Services, Inc., I propose the following analytical parameter guidelines be used to define "unadulterated fossil fuel" for used oil air toxic regulation permit review determinations.

Constituent/Property	Allowable Level
Arsenic	1 ppm maximum
Cadmium	2 ppm maximum
Chromium	5 рр и ма хішищ
Lead	100 ppm maximum
Total Halogens	1000 ppm maximum
Flash Point	100° f minimum
Sulfur	1.0%
Ash	1.0%

References: * Federal Register Volume 50, page 49205 11/29/85

* EPA 450/2-88-006a

Technical Laboratories, Inc.; analyses

ASTM D396-80

Note: Neither new or existing permitted sources are exempt from Prevention of Significant Deterioration (PSD) review requirements.

cc: Laura Butler Russell Hageman Sandra Birckhead Sammy Amerson Mike Aldridge

Revised, June 11, 1991

Drum-Tanker-Rail Car Coliwasa

Our newest disposable sampler is designed to extract samples from drums, tanks, and rail cars. The 7/8" diameter samplers are manufactured from HDPE and come in lengths of 42" and 7'.

The sampler is quick and easy to use. Just insert the sampler into the drum or tank to be sampled, pull up on the handle to lock the sample in place, remove the sampler from the tank and push down on the handle to release the sample. The sampler can also be used to sample at a specific depth by closing the valve before inserting the sampler and opening the valve by pushing down on the handle to open the valve once the desired sampling depth has been reached.

Unlike other samplers which require the operator to hold the valve closed, the unique design of our sampler holds the valve assembly closed allowing the operator to use one hand or both hands to remove the sampler from the tank.

When sampling from full containers, our 42" sampler will extract a 250 ml sample, and our 7' sampler will extract a 500 ml sample.

Catalog Number	<u>Description</u>	Case Pack
5665	42" Drum sampler	12
5665C	42" Drum sampler - precleaned	12
5670	42" Drum sampler	24
5670C	42" drum sampler - precieaned	24
5680	7' Tank truck sampler	

Quickie Sampler

Our 48 inch polyethylene sampler is designed to extract samples from drums and tanks directly into a bottle and is manufactured to fit easily through the opening of a standard 55 gallon drum. The sampler is quick and easy to use. Just screw the bottle into the lower end of the sampler, lower the sampler into the drum or tank, and the bottle is filled automatically. The sampler is supplied complete with one 125 ml sampling bottle.

Catalog number 5240

Quickie Sampler 125 ML Sampling Bottle
Packaged 24 per case.
Catalog number 9084

Short Glass Drum Thief

Our newest drum thief is specifically designed to take liquid samples from small containers.

Manufactured from 9mm, 12mm or 16mm glass tubing, these thieves are only

18" long and are designed to extract samples from containers such as jars, bottles, gallon jugs, and paint cans.

Packaged 50 per case.

Catalog Number	<u>Size</u>	Approximate Volume
5526	9mm	20 ml
5527	12mm	40 ml
5528	16mm	60 ml

Polyethylene Drum Thief

This economical sampler is ideal for field usage where a glass sampler might present a breakage problem or, in any sampling operation where an inert plastic sampler is required or preferred.

Each polyethylene drum thief is 42" long and is manufactured from virgin HDPE. Unlike other plastic samplers which are manufactured using a cost saving thin wall, the CONBAR op polyethylene drum samplers have a heavy wall which allows them to be sealed much easier during sampling.

12mm (.450) OD 50 ml (1 1/2 oz.) capacity

Catalog Number	Case Fack
2405	25
2404C	25
2410	50
2415	100

16mm (.625) OD 150 ml (5 oz.) capacity

Catalog Number	Case Pack
2440	25
2440C	25
2445	50
2450	100

DIVISION OF AIR QUALITY RECYCLED OIL SAMPLE REPORT

Sample #:	Date:	Time:
Facility ID:	Permit Number:	
Facility Name:		
Sample Point Description:		
Sample Device Used:		
Recycled Oil Supplier General Information Name: Address: City:		
Batch analytical results of recycled oil from (If no, explain.)		no
Analyze for: Sulfur Flash Point Vis As Cd Cr Pb Sp. Gravity Moisture All Parameters (PCE	Ash BTU Total Halogens	
Sample Type: #2 oil #4 oil	#6 oil other	
Received by (Please Print):Signature:		
Remarks:		
Inspector Name (Please Print):		
Inspector Signature:		

Division of Air Quality Air Toxics Protection Branch CHAIN OF CUSTODY

			Sample I	Sample Information			
Facility:			COC sealed by:	l by:	Date:		Time:
Sampling Site:			COC broken by:	n by:	Date:		Time:
Comments:							
Sample No.	COC No.	Zo.		Sample shipped to:	ed to:	Ω	Date shipped:
			Transfer	Transfer Information			
	Relinquished by				Relinquished to		
Printed Name	Signature	Date	Time	Printed Name	Signature		Date Time

North Carolina Dept. of Environment & Natural Resources Division of Air Quality / Toxics Laboratory

4403 Reedy Creck Road Raleigh, NC 27607 (919) 733-9777



Standard Practice for Sampling With a Composite Liquid Waste Sampler (COLIWASA)¹

This summend is issued under the fixed designation D 5495; the number intracetizately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number to parentheses indicates the year of last revision. A number to parentheses indicates the year of last retrigion or reapproval.

Scope

1.1 This practice describes the procedure for sampling liquids with the composite liquid waste sampler, or "COLIWASA." The COLIWASA is an appropriate device for obtaining a representative sample from stratified or unstratified liquids. Its most common use is for sampling containerized liquids, such as tanks, barrels, and drums. It may also be used for pools and other open bodies of stagnant liquid.

NOTE—A limitation of the COLIWASA is that the stopper mechanism may not allow collection of approximately the bottom inch of material, depending on construction of the stopper.

1.2 The COLIWASA should not be used to sample flowing or moving liquids.

1.3 This standard does not purport to address all of the sajety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards:

D 4687 Guide for General Planning of Waste Sampling² D 5088 Practice for Decontamination of Field Equipment

Used at Nonradioactive Waste Sites³

D 5283 Practice for Generation of Environmental Data Related to Waste Management Activities: Quality Assurance and Quality Control Planning and Implementation²

3. Summary of Practice

3.1 A clean device is slowly lowered into the liquid to be sampled. After it has filled, the bottom of the sampling tube is closed and the device is retrieved. The contents are subsequently discharged into a sample container.

4. Significance and Use

4.1 This practice is applicable to sampling liquid wastes and other stratified liquids. The COLIWASA is used to obtain a vertical column of liquid representing an accurate cross-section of the sampled material. To obtain a representative sample of stratified liquids, the COLIWASA should be open at both ends so that material flows through it as it is slowly lowered to the desired sampling depth. The COLIWASA must not be lowered with the stopper in place. Opening the stopper after the tube is submerged will cause material to flow in from the bottom layer only, resulting in gross over-representation of that layer.

4.2 This practice is to be used by personnel acquiring samples.

4.3 This practice should be used in conjunction with Guide D 4687 which covers sampling plans, safety, QA, preservation, decontamination, labeling and chain-of-custody procedures; Practice D 5088 which covers decontamination of field equipment used at waste sites, and Practice E 5283 which covers project, specifications and practices for environmental field operations.

5. Sampling Equipment

5.1 COLIWASA's are available commercially with different types of stoppers and locking mechanisms, but they all operate using the same principle. They can also be constructed from materials such as polyvinylchloride (PVC), glass, metal, or polytetrafluoroethylene (PTFE). A traditional model of the COLIWASA is shown in Fig. 1 [de Vera et al.]*; however, the design can be modified or adapted, or both, to meet the needs of the sampler. COLIWASA's must be selected that are constructed of materials compatible with the waste being sampled and with the analyses or tests to be performed. Due to the unknown nature of most containerized liquid wastes, COLIWASA's made of glass or polytetrafluoroethylene are best for general use.

Sample Containers

6.1 Plastic, glass or other nonreactive containers should be used. Refer to Guide D 4687 for further information on containers.

7. Procedure

7.1 Make certain the COLIWASA is clean and functioning properly. It is essential that the stopper at the bottom of the sampling tube closes securely.

7.2 Open the COLIWASA by placing the stopper mechanism in the open position.

7.3 Lower the COLIWASA into the liquid slowly so that

¹ This practice is under the jurisdiction of ASTM Committee D-34 on Wassa Management and it the direct responsibility of Subcommittee D34.01 on Sampling and Monitoring.

Current edition approved Jan. 15, 1994, Published March 1994,

Amusi Book of ASTM Standards, Vol. 11.04.
Annual Book of ASTM Standards, Vol. 04.04.

^{*}de Vera. E. R., Siamons, S. P., Stapoens, R. C., and Storm, D. L., "Samplers and Sampling Procedures for Hazardous Wester Streams," EPA-500/2-80-018, January 1980.

^{*} Ford, P. J., Turins, P. J., and Seriey, O. E., *Characterization of Hamiltons Wasse Sites—A Methods Manual: Volume II.* Available Sampling Meshods. Second Edition, EPA-600/4-84-076, December 1994.

D 5495

Pipe, FVC, translocant, 4.13cm (1 5/8") I.O., 4.76cm (1 7/8") O.D.

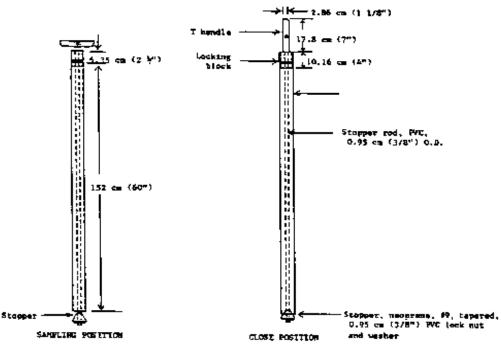


FIG. 1 Composite Liquid Waste Sampler (COLIWASA) (Typical)

the levels of the liquid inside and outside the sampler tube remain about the same. If the level of the liquid in the sample tube is lower than that outside the sampler, the sampling tate is too fast and a nonrepresentative sample will result

- 7.4 Use the stopper mechanism to close the COLIWASA when it reaches the desired depth in the liquid.
- 7.5 Withdraw the sampler from the liquid with one hand while wiping the sampler tube with a disposable cloth or rag with the other hand.
 - 7.6 Carefully discharge the sample into a suitable con-

tainer by slowly opening the stopper mechanism while the lower end of the COLIWASA is positioned in the sample container.

- 7.7 Seal the sample container; attach the label and seal; record in the field logbook; and complete the chain-of-custody record.
- 7.8 Decontaminate the used equipment in accordance with Practice D 5088.

8. Keywords

COLIWASA; drum sampling; liquid sampling; sampling; waste

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every live years and if not revised, either reapproved or entirities. Your comments are invited either for revision of the standards and should be addressed to ASTM Headcostrais. Your comments will receive careful consideration at a meeting of the responsible recriminal committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards. 1916 Rece St., Philadelphia, PA 19103.



North Carolina Department of Environment and Natural Resources

Division of Air Quality

Michael F. Easley, Governor

William G. Ross, Jr., Secretary B. Keith Overcash P. E., Director

May 3, 2005

XXXXXXXXXXX Street or Road City, State ZIP

Subject: Notice of Enforcement Policy - Recycled Oil Combustion

Dear XXX:

This letter provides information regarding a change in the Enforcement policy of the North Carolina Division of Air Quality (DAQ) with regards to the Recycled Oil Management Plan (referred to as "Plan"). In an effort to reduce waste and maximize resources, the DAQ implemented the Recycled Oil Management Plan in December 1999. The purpose of the Plan is to provide a mechanism by which vendors, combustors or generators of previously used oil can demonstrate equivalency to unadulterated No. 2 and No. 4 oils by meeting typical constituent levels for an interim period of time until you otherwise make an air toxics demonstration. The following compounds are addressed in the Plan: arsenic, cadmium, chromium, lead, total halogens, sulfur and ash (see attachment 1). Liability for combusting waste oil not meeting the specified levels for these compounds resides with the facility that is actually burning the oil:

- Only oil generated on site, or oil purchased from an "Approved Recycled Oil Supplier" may be combusted.
- In either case, an air quality permit allowing the combustion of recycled oil is required.
- Oil generated on-site in total annual quantities below 500 gallons are not required to follow Plan requirements for demonstrating equivalency, but do need to document their activity.
- Oil generated on-site in total quantities over 500 gallons annually must follow Plan requirements for demonstrating equivalency prior to combustion. The analytical report(s) documenting equivalency must be available.
- Each <u>shipment</u> of recycled oil from an approved supplier must be accompanied by the analytical report demonstrating its equivalency with the unadulterated oil constituent levels. It is the responsibility of the combustion source to obtain this documentation and to check each constituent to ensure that the shipment meets their air quality permits which incorporates the Plan requirements *prior* to combustion. Generic statements from the supplier are not acceptable.
- Burning oil shipments without this documentation is considered a violation of the air quality permit and will result in enforcement action.

- Burning oil shipments where documentation shows that equivalency has not been met is considered a violation of the air quality permit and will result in enforcement action.
- The DAQ periodically samples facilities combusting recycled oil and performs laboratory analysis

Since implementation, DAQ has identified several instances where it appears that the constituent levels had been exceeded in oil samples that were collected at facilities receiving oil from approved vendors. In the past, DAQ's procedures were to collect a second sample from these same facilities within one year decisions regarding enforcement action were then made based on the subsequent sample. This will no longer be the procedure. Now, during the DAQ audit, when an oil sample is identified as not meeting the equivalency criteria as specified in your air quality permit, a NOTICE of VIOLATION will be issued to the facility combusting the oil even if the approved supplier has provided you an analysis, which indicates that the recycled oil shipment was in compliance with the unadulterated oil specifications. It should be noted that all audit samples will be collected as close as possible to the burner.

In addition to sampling combustion sources, the DAQ will begin collecting inspection samples from the Approved Recycled Oil Suppliers. Oil samples that fail the audit may result in revocation of a supplier's approval. Additionally, the DAQ is evaluating the feasibility of a rule change, which may make it illegal in North Carolina to supply recycled oil not meeting specific criteria. In the interim, facilities combusting recycled oil contrary to the terms and conditions of their air permits will be held solely liable for violating North Carolina's Air Quality Rules. Please discuss this issue with your recycled oil supplier and take all steps necessary to avoid potential violations at your facility. One step you may wish to consider is to install car-seals or similar "lock-out/tag-out" devices on the waste oil tank fill and retain records that indicate when the seal is broken. Each broken seal event should reference a particular delivery and that delivery's supplier analysis. Should you have questions regarding this matter, please contact the Compliance Coordinator in your regional DAQ office.

Sincerely,

Lee A. Daniel, Chief Technical Services Section

CC: Regional Supervisors

Regional Compliance Coordinators

Example Form of Recycled Oil Analytical Report and Batch Signature Information

LITY NAME	FACILITY CITY
LITY COUNTY	FUEL OIL NUMBER
OOR/PROCESSOR NAME	SAMPLE NUMBER
CERTIFICATION ATTACHED: _	BATCH NUMBER:
CH VOLUME (GAL)	PROCESSING TANK NUMBER:
E /TIME BATCH COMPLETED TRE	ATEMENT:
YCLED OIL VOLUME DELIVERED	TO FACILITY (GAL):
E/TIME OF DELIVERY TO FACILI	ГҮ:
NC I PARAMETER LIM	RECYCLED OIL IT SAMPLE CONCENTRATION ²
ARSENIC (ppmw)	1.0
CADMIUM ppmw)	2.0
CHROMIUM (ppmw)	5.0
LEAD (ppmw)	100
TOTAL HALOGENS (ppmw)	1000
SULFUR (%weight basis)	
- No. 2	0.50
- No. 4, 5, or 6	2.0
ASH (%weight basis)	1.0
FLASH POINT (°F) (Minimim)	
- No. 2	100
- No. 4	130
- No. 5 or 6	175
	Forth Carolina Air Toxics regulations, except where specified as minimum eter 1 – 7 are on a weight basis.
2 = Analyte concentration expres	ssed as ppmw or micrograms per gram), wt/wt, of sample.
Notes:	

NORTH CAROLINA APPROVED LIST OF RECYCLED OIL SUPPLIERS

as of **January 28, 2013**

Company	Grade	Approved Date	Re-Certified Date
Enterprise Oil 5201 N. Middlebrook Pike Knoxville, Tennessee 37921 Contact: Charles Alexander B Phone: (800) 875-3860 or (865) 558-0533	No. 4	12/95	11/18/2009
Holston Group, Inc. 19119 Great Smoky Mt. Expressway Waynesville, North Carolina 28786 Contact: Roger Wilson Phone: (800) 222-4530	No.2 No. 4	10/93	4/28/2009
Necessary Oil Company 1300 Georgia Ave. Bristol, Tennessee 37620 Contact: Joe Byington Phone: (423) 764-4533	No. 4	12/94	11/17/2009
Noble Oil Services, Inc. 5617 Clyde Rhyne Drive Sanford, North Carolina 27330 Contact: Jim Noble Phone: (919) 774-8180	No. 2	6/91	1/2009
Noble Oil Services, Inc. 5617 Clyde Rhyne Drive Sanford, North Carolina 27330 Contact: Jim Noble Phone: (919) 774-8180	No. 4	6/99	1/2009
Safety-Kleen System Inc. 12040 Goodrich Drive Charlotte, North Carolina 28273 Contact: Richard Stout Phone: (704) 201-2002 E-mail: Richard.Stout@safety-kleen.com	No. 4	3/97	6/23/2009

Company	Grade	Approved Date	Re-Certified Date
Safety-Kleen System Inc. 12040 Goodrich Drive Charlotte, North Carolina 28273 Contact: Richard Stout Phone: (704) 201-2002 E-mail: Richard.Stout@safety-kleen.com	No. 2	12/08/98	6/23/2009
Safety-Kleen System Inc. 2760 Valley View Drive Shreveport, Louisiana 71108 Contact: Brian Dick Phone: (318) 688-1191	No.4	7/3/02	6/23/2009
FCC Environmental 2115 Speedrail Court Concord, North Carolina 28025 Contact: Bill Henkel Phone: (704) 455-1333 x 24	No. 2 No. 4	5/93	7/14/2009
FCC Environmental 5800 Farrington Avenue Alexandria, Virginia 22304-4893 Contact: Drew Frye Phone: (800) 673-8521 or (703) 370-7306 FAX: (703) 370-8067	No. 4	1/16/98	7/14/2009
Shamrock Environmental Corporation P.O. Box 14987 Greensboro, North Carolina 27415 Contact: Jim Hollingsworth Phone: (336) 375-1989 FAX: (336) 375-1801	No. 4	7/3/02	8/2009
Universal Environmental Services, LLC 411 Dividend Drive Peachtree City, Georgia 30269 Contact: Donald Golden Phone: (770) 486-8816 FAX: (770) 486-0616 E-mail: Jim.Hollingsworth@shamrockenviro.com	No. 2	12/17/04	11/2009

Company	Grade	Approved Date	Re-Certified Date
Advanced Oil 1257 Henrico Road Conley, Georgia 30288-1005 Contact: Laurie Whittington Phone: (404) 361-3811 FAX (404) 361-1788	No. 4	5/31/05	10/2009
FCC Environmental 2353 Lanier Road Rockville, Virginia 23146 Contact: Ron Heath Phone: (804) 749-8344x205 FAX: (804) 749-8450	No. 4	5/29/08	
FCC Environmental 5539 Faris Street Norfolk, Virginia 23531 Contact: Rob Helgeson Phone: (757) 852-9142 FAX: (757) 852 – 9246	No. 4	5/29/08	
VLS Recovery Service 305 South Main Street Mauldin, SC 29662 Contact: Platt Moore Phone:(864) 962-9953 Ext 314 FAX: (864) 679-3703 E-mail: platt.moore@vlsrs.com	No.4	12/03/08	
Coastal Refining Corporation 2830 Tremont Road Savannah, Georgia 31405 Contact: Richard L. Glendye, Jr. Phone: (912) 233-9999 FAX: (912) 236-4162	No.5	1/23/2009	
HAZ-MAT Environmental Services 221 Dalton Avenue Charlotte, NC 28206 Contact: Neil Danziger- Phone: (704) 332-5600 FAX:(704) 375-7183 E-mail: neil@hazmatnc.com	No.2 No.4	5/6/2009	

Company	Grade	Approved Date	Re-Certified Date
Sully's Oil Recovery			
10518 Royster Road NE	No. 2	12/04/2012	
Post Office Box 656			
Leland, North Carolina 28451			
Contact: Scott Sutherland			
Phone:(910) 371-5792			

North Carolina Division of Air Quality

RECYCLED OIL PERMITTING PROCEDURES

Facilities wishing to combust recycled oil, obtained from an approved vendor, must comply with the following procedures:

- Submit a permit modification to the regional or central office, with the appropriate fee, prior to combustion of the product. (Note that this is a change in the used oil procedures.)
- The application must include a request to combust the vendor-approved recycled oil. The combustion of this product should be treated as the combustion of unadulterated fuel oil and as such should not be considered a "modification" under the NC air toxics program. In addition, in most cases the switch from virgin unadulterated fuel to equivalent recycled oil will not be considered a modification under the Prevention of Significant Deterioration (PSD) program. Reference PSD regulations contained in 40 CFR 51.166 for further details.
- The item description within the permit should also be modified to describe the units ability to combust this fuel. (E.g. one No. 2 fuel oil/recycled "Fuel Grade" (e.g. No. 2) oil-fired boiler (30 million Btu per bour, ID No. B-1).

Example:

one No. 2 fuel oil/recycled No. 2 oil-fired boiler

(30 million Btu per hour, ID No. B-1).

4) The permit should be issued with the following permit condition (with modification as necessary for various fuel oils - this example is for No. 2):

The latest recycled oil stipulation:

Note, for No. 4 fuel oil, the minimum flash point is 135°F, and a maximum 2.0 % S. Note, for No. 5 or 6 fuel, the minimum flash point is 175°F, and a maximum 2.0 % S.

- <u>RECYCLED NO. 2 FUEL OIL REQUIREMENTS</u> The Permittee is allowed to burn recycled No. 2 fuel oil supplied by a DAQ-approved vendor as follows:
 - a. <u>Specifications</u> The recycled No. 2 fuel oil shall be equivalent to unadulterated fossil fuel by meeting the following criteria:

Constituent/Property	Allowable Level	
Arsenic	1 ррт тахітит	
Cadmium	2 ppm maximum	
Chromium	5 ppm maximum	
Lead	титіхит тада ОО1	
Total Halogens	1000 ppm maximum	
Flash Point	100°F miaimum	
Sulfur	0.5% maximum (by weight)	
Ash	1.0 % maximum	

The Permittee is responsible for ensuring that the recycled No. 2 fuel oil meets the approved criteria for unadulterated fuel. The Permittee is held responsible for any discrepancies discovered by DAQ as a result of any sampling and analysis of the fuel oil.

- b. <u>Recordkeeping Requirements</u> The Permittee shall maintain at the facility for a minimum of three years, and shall make available to representatives of the DAQ upon request, accurate records of the following:
 - the actual amount of recycled No. 2 fuel oil delivered to, and combusted at, the facility on an annual basis.
 - the results of any analytical testing of the recycled No. 2 fuel oil as it is sampled and tested by the vendor.
- Reporting Requirements Within 30 days after each calendar year, the Permittee shall submit in writing to the Regional Supervisor, DAQ, the following:
 - a summary of the results of any analytical testing for the previous 12 months.
 - the total gallons of recycled No. 2 fuel oil from each approved vendor combusted at the facility for the previous 12 months.
- d. The DAQ reserves the right to require additional testing and/or monitoring of the recycled No. 2 fuel oil on an annual basis or without notice.



NCDENR

North Carolina Department of Environment and Natural Resources Division of Air Quality

Michael F. Easley, Governor

William G. Ross, Jr., Secretary B. Keith Overcash, P.E., Director

May 28, 2004

MEMORANDUM

To: DAQ Section Chiefs

DAQ Regional Supervisors

From: Keith Overcash, P.E.

Subject: On-site Generated Waste Oil Combustion

The DAQ currently has in place procedures that allow sources in North Carolina to burn waste oils which have been deemed "unadulterated". These waste oil procedures were designed to address large to medium sized shipments of waste oil by suppliers, like Noble Oil Services, to manufacturing sites for use as fuel. The requirements set up under this procedure include relatively frequent and complex sampling and monitoring. Such requirements are reasonable for sources that burn large quantities of this product because when a facility burns large quantities of waste oil a potential for increased toxic air pollutant (TAP) emissions exists if the product cannot be ensured to be equivalent to unadulterated fuels.

On the other hand, the current procedure does not address small quantities of waste oil such as those generated by on-site mechanical activities. When dealing with such smaller quantities, the risk should be reduced and, therefore, the resulting regulatory regime governing such activity can in most cases be safely mitigated. This is because the amount of waste oils generated and burned are minimal as compared with the total quantity of fuel typically burned at these facilities. From an environmental viewpoint, the dilution of the on-site waste oil with a small amount of virgin fuel will quickly reduce the level of TAPs emitted to well below the specifications we have developed to define unadulterated recycled waste oil. Additionally, in the case of waste oil suppliers like Noble Oil, the product that is burned is a conglomeration of oils collected from various locations and applications. In contrast, where a source burns relatively small amounts of a waste oil generated from known and limited on-site sources, the risk of contamination and adverse environmental impact is greatly reduced.

Based on these considerations, sources burning lesser quantities of on-site generated waste oil should be able to do so through a second tier permitting approach. Using this approach, the source is not required to obtain an air permit to burn on-site generated waste oil provided not more than 500 gallons are burned in any single year.

On-site Generated Waste Oil Combustion May 28, 2004

Most facilities within North Carolina have relatively small combustion sources, on the order of a total of 30 million Btu per hour heat input. Based on this relatively small size, annual waste oil combustion of 500 gallons would represent less than 0.1 percent of the total annual fuel oil usage. This low percentage allows facilities in North Carolina to dispose of relatively small amounts of on-site generated waste oil in an effective, efficient manner with a low risk of adverse environmental effects.

It should be noted that although the division may now allow on-site generated waste oils to be burned without the more structured regulatory scheme associated with the large quantity generators, the division still retains the right to test the oil or request that the company test it if we are concerned, based on reasonable suspicion, that the as-burned oil may represent a more significant risk.

jwe

cc: D. R. van der Vaart

Michael Aldridge

Lori Cherry

Local Programs

METHOD 3052

MICROWAVE ASSISTED ACID DIGESTION OF SILICEOUS AND ORGANICALLY BASED MATRICES

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the microwave assisted acid digestion of siliceous matrices, and organic matrices and other complex matrices. If a total decomposition analysis (relative to the target analyte list) is required, the following matrices can be digested: ashes, biological tissues, oils, oil contaminated soils, sediments, sludges, and soils. This method is applicable for the following elements:

Aluminum	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Boron	Cobalt	Manganese	Selenium	Vanadium
Barium	Copper	Mercury	Silver	Zinc
Beryllium		•		

Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest (see Sec.8.0).

Note: This technique is not appropriate for regulatory applications that require the use of leachate preparations (i.e., Method 3050, Method 3051, Method 1311, Method 1312, Method 1310, Method 1320, Method 1330, Method 3031, Method 3040). This method is appropriate for those applications requiring a total decomposition for research purposes (i.e., geological studies, mass balances, analysis of Standard Reference Materials) or in response to a regulation that requires total sample decomposition.

- 1.2 This method is provided as a rapid multi-element, microwave assisted acid digestion prior to analysis protocol so that decisions can be made about the site or material. Digests and alternative procedures produced by the method are suitable for analysis by flame atomic absorption spectrometry (FLAA), cold vapor atomic absorption spectrometry (CVAA), graphite furnace atomic absorption spectrometry (GFAA), inductively coupled plasma atomic emission spectrometry (ICPAES),inductively coupled plasma mass spectrometry (ICP-MS) and other analytical elemental analysis techniques where applicable. Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to this manual's "Disclaimer" when conducting analyses using Method 3052.
- 1.3 The goal of this method is total sample decomposition and with judicious choice of acid combinations this is achievable for most matrices (see Sec. 3.2). Selection of reagents which give the highest recoveries for the target analytes is considered the optimum method condition.

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December 1996

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is digested in 9 mL of concentrated nitric acid and usually 3 mL hydrofluoric acid for 15 minutes using microwave heating with a suitable laboratory microwave system. The method has several additional alternative acid and reagent combinations including hydrochloric acid and hydrogen peroxide. The method has provisions for scaling up the sample size to a maximum of 1.0 g. The sample and acid are placed in suitably inert polymeric microwave vessels. The vessel is sealed and heated in the microwave system. The temperature profile is specified to permit specific reactions and incorporates reaching 180 \pm 5 °C in approximately less than 5.5 minutes and remaining at 180 \pm 5 °C for 9.5 minutes for the completion of specific reactions (Ref. 1, 2, 3, 4). After cooling, the vessel contents may be filtered, centrifuged, or allowed to settle and then decanted, diluted to volume, and analyzed by the appropriate SW-846 method.

3.0 INTERFERENCES

- 3.1 Gaseous digestion reaction products, very reactive, or volatile materials that may create high pressures when heated and may cause venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples,may cause enough pressure to vent the vessel if the sample size is greater than 0.25 g. Variations of the method due to very reactive materials are specifically addressed in sections 7.3.4 and 7.3.6.1.
- 3.2 Most samples will be totally dissolved by this method with judicious choice of the acid combinations. A few refractory sample matrix compounds, such as TiO2, alumina, and other oxides may not be totally dissolved and in some cases may sequester target analyte elements.
- 3.3 The use of several digestion reagents that are necessary to either completely decompose the matrix or to stabilize specific elements may limit the use of specific analytical instrumentation methods. Hydrochloric acid is known to interfere with some instrumental analysis methods such as flame atomic absorption (FLAA) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The presence of hydrochloric acid may be problematic for graphite furnace atomic absorption (GFAA) and inductively coupled plasma mass spectrometry (ICP-MS). Hydrofluoric acid, which is capable of dissolving silicates, may require the removal of excess hydrofluoric acid or the use of specialized non-glass components during instrumental analysis. Method 3052 enables the analyst to select other decomposition reagents that may also cause problems with instrumental analyses necessitating matrix matching of standards to account for viscosity and chemical differences.

4.0 APPARATUS AND MATERIALS

- 4.1 Microwave apparatus requirements.
- 4.1.1 The temperature performance requirements necessitate the microwave decomposition system sense the temperature to within \pm 2.5EC and automatically adjust the microwave field output power within 2 seconds of sensing. Temperature sensors should be accurate to \pm 2EC (including the final reaction temperature of 180EC). Temperature feedback control provides the primary control performance mechanism for the method. Due to the flexibility in the reagents used to achieve total analysis, tempertuare feedback control is necessary for reproducible microwave heating.

Alternatively, for a specific set of reagent(s) combination(s), quantity, and specific vessel type, a calibration control mechanism can be developed similar to previous microwave methods (see Method 3051). Through calibration of the microwave power, vessel load and heat loss, the reaction temperature profile described in Section 7.3.6 can be reproduced. The calibration settings are specific for the number and type of vessel used and for the microwave system in addition to the variation in reagent combinations. Therefore no specific calibration settings are provided in this method. These settings may be developed by using temperature monitoring equipment for each specific set of equipment and reagent combination. They may only be used if not altered as previously described in other methods such as 3051 and 3015. In this circumstance, the microwave system provides programmable power which can be programmed to within ± 12 W of the required power. Typical systems provide a nominal 600 W to 1200 W of power (Ref. 1, 2, 5). Calibration control provides backward compatibility with older laboratory microwave systems without temperature monitoring or feedback control and with lower cost microwave systems for some repetitive analyses. Older lower pressure vessels may not be compatible.

4.1.2 The temperature measurement system should be periodically calibrated at an elevated temperature. Pour silicon oil (a high temperature oil into a beaker and adequately stirred to ensure a homogeneous temperature. Place the microwave temperature sensor and a calibrated external temperature measurement sensor into the beaker. Heat the beaker to a constant temperature of $180 \pm 5^{\circ}$ C. Measure the temperature with both sensors. If the measured temperatures vary by more than $1 - 2^{\circ}$ C, the microwave temperature measurement system needs to be calibrated. Consult the microwave manufacturer's instructions about the specific temperature sensor calibration procedure.

CAUTION: The use of microwave equipment with temperature feedback control is required to control the unfamiliar reactions of unique or untested reagent combinations of unknown samples. These tests may require additional vessel requirements such as increased pressure capabilities.

4.1.3 The microwave unit cavity is corrosion resistant and well ventilated. All electronics are protected against corrosion for safe operation.

CAUTION: There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. A listing of these specific suggestions is beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer, and literature for proper and safe operation of the microwave equipment and vessels.

4.1.4 The method requires essentially microwave transparent and reagent resistant suitably inert polymeric materials (examples are PFA or TFM suitably inert polymeric polymers) to contain acids and samples. For higher pressure capabilities the vessel may be contained within layers of different microwave transparent materials for strength, durability, and safety. The vessels internal volume should be at least 45 mL, capable of withstanding pressures of at least 30 atm (30 bar or 435 psi), and capable of controlled pressure relief. These specifications are to provide an appropriate, safe, and durable reaction vessel of which there are many adequate designs by many suppliers.

CAUTION: The outer layers of vessels are frequently not as acid or reagent resistant as the liner material and must not be chemically degraded or physically damaged to retain the performance and safety required. Routine examination of the vessel materials may be required to ensure their safe use.

CAUTION: The second safety concern relates to the use of sealed containers without pressure relief devices. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures, but must be safely contained. However, many digestion vessels constructed from certain suitably inert polymerics may crack, burst, or explode in the unit under certain pressures. Only suitably inert polymeric (such as PFA or TFM and others) containers with pressure relief mechanisms or containers with suitably inert polymeric liners and pressure relief mechanisms are considered acceptable.

Users are therefore advised not to use domestic (kitchen) type microwave ovens or to use inappropriate sealed containers without pressure relief for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details, consult Reference 3 and 6.

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within most systems (Ref. 1). The speed of the turntable should be a minimum of 3 rpm.

CAUTION: Laboratories should not use domestic (kitchen) type microwave ovens for this method. There are several significant safety issues. First, when an acid such as nitric is used to effect sample digestion in microwave units in open vessel(s), or sealed vessels equipment, there is the potential for the acid gas vapor released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a system with isolated and corrosion resistant safety devices prevents this from occurring.

- 4.2 Volumetric ware, volumetric flasks, and graduated cylinders, 50 and 100 mL capacity or equivalent.
- 4.3 Filter paper, qualitative or equivalent.
- 4.4 Filter funnel, polypropylene, polyethylene or equivalent.
- 4.5 Analytical balance, of appropriate capacity, with a \pm 0.0001 g or appropriate precision for the weighing of the sample. Optionally, the vessel with sample and reagents may be weighed, with an appropriate precision balance, before and after microwave processing to evaluate the seal integrity in some vessel types.

5.0 REAGENTS

5.1 All reagents should be of appropriate purity or high purity (acids for example, should be sub-boiling distilled where possible) to minimize the blank levels due to elemental contamination. All references to water in the method refer to reagent water (Ref. 7). Other reagent grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.
- 6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Sec. 3.1.3 of this manual, for further information.
 - 6.3 Refer to Chapter Three for the appropriate holding times and storage conditions.

7.0 PROCEDURE

- 7.1 Temperature control of closed vessel microwave instruments provides the main feedback control performance mechanism for the method. Control requires a temperature sensor in one or more vessels during the entire decomposition. The microwave decomposition system should sense the temperature to within \pm 2.5 C and permit adjustment of the microwave output power within 2 seconds.
- 7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels (fluoropolymer liners only) should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80 C, but less than boiling) for a minimum of two hours followed with o hot (1:1) nitric acid (greater than 80 C, but less than boiling) for a minimum of two hours and rinsed o with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware (not used with HF) and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh a well-mixed sample to the nearest 0.001 g into an appropriate vessel equipped with a pressure relief mechanism. For soils, ash, sediments, sludges, and siliceous wastes, initially use no more than 0.5 g. For oil or oil contaminated soils, initially use no more than 0.25 g.

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 $7.3.2~{\rm Add}~9\pm0.1~{\rm mL}$ concentrated nitric acid and $3\pm0.1~{\rm mL}$ concentrated hydrofluoric acid to the vessel in a fume hood. If the approximate silicon dioxide content of the sample is known, the quantity of hydrofluoric acid may be varied from 0 to 5 mL for stoichiometric reasons. Samples with higher concentrations of silicon dioxide (> 70%) may require higher concentrations of hydrofluoric acid (>3 mL HF). Alternatively samples with lower concentrations of silicon dioxide (< 10% to 0%) may require much less hydrofluoric acid (0.5 mL to 0 mL). Examples are presented in Table 1, 2, 3, and 6. Acid digestion reagent combinations used in the analysis of several matrices, listed in Table 7, provide guidance for the development of new matrix decomposition procedures.

7.3.3 The addition of other reagents with the original acids prior to digestion may permit more complete oxidation of organic sample constituents, address specific decomposition chemistry requirements, or address specific elemental stability and solubility problems.

The addition of 2 ± 2 mL concentrated hydrochloric acid to the nitric and hydrofluoric acids is appropriate for the stabilization of Ag, Ba, and Sb and high concentrations of Fe and Al in solution. The amount of HCl needed will vary depending on the matrix and the concentration of the analytes. The addition of hydrochloric acid may; however, limit the techniques or increase the difficulties of analysis. Examples are presented in Table 4.

The addition of hydrogen peroxide (30%) in small or catalytic quantities (such as 0.1 to 2 mL) may aid in the complete oxidation of organic matter.

The addition of water (double deionized) may (0 to 5 mL) improve the solubility of minerals and prevent temperature spikes due to exothermic reactions.

NOTE: Supporting documentation for the chemistry of this method has been prepared in chapters 2 and 3 of reference 3. It provides additional guidance and documentation of appropriate reagent, matrix and analyte combinations that can be employed in this method.

CAUTION: Only one acid mixture or quantity may be used in a single batch in the microwave to insure consistent reaction conditions between all vessels and monitored conditions. This limitation is due to the current practice of monitoring a representative vessel and applying a uniform microwave field to reproduce these reaction conditions within a group of vessels being simultaneously heated.

CAUTION: Toxic nitrogen oxide(s), hydrogen fluoride, and toxic chlorine (from the addition of hydrochloric acid) fumes are usually produced during digestion. Therefore, all steps involving open or the opening of microwave vessels must be performed in a properly operating fume ventilation system.

CAUTION: The analyst should wear protective gloves and face protection and must not at any time permit a solution containing hydrofluoric acid to come in contact with skin or lungs.

CAUTION: The addition of hydrochloric acid must be from concentrated hydrochloric acid and not from a premixed combination of acids as a buildup of toxic chlorine and possibly other gases will result from a premixed acid solution. This will over pressurize the vessel due to the release of these gases from solution upon heating. The gas effect is greatly lessened by following this suggestion.

CAUTION: When digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 0.25 g can be used.

CAUTION: The addition of hydrogen peroxide should only be done when the reactive components of the sample are known. Hydrogen peroxide may react rapidly and violently on easily oxidizable materials and should not be added if the sample may contain large quantities of easily oxidizable organic constituents.

- 7.3.4 The analyst should be aware of the potential for a vigorous reaction. If a vigorous reaction occurs upon the initial addition of reagent or the sample is suspected of containing easily oxidizable materials, allow the sample to predigest in the uncapped digestion vessel. Heat may be added in this step for safety considerations (for example the rapid release of carbon dioxide from carbonates, easily oxidized organic matter, etc.). Once the initial reaction has ceased, the sample may continue through the digestion procedure.
- 7.3.5 Seal the vessel according to the manufacturer's directions. Properly place the vessel in the microwave system according to the manufacturer's recommended specifications and connect appropriate temperature and pressure sensors to vessels according to manufacturer's specifications.
- 7.3.6 This method is a performance based method, designed to achieve or approach total decomposition of the sample through achieving specific reaction conditions. The temperature of each sample should rise to 180 ± 5 °C in approximately 5.5 minutes and remain at 180 ± 5 °C for 9.5 minutes. The temperature-time and pressure-time profile are given for a standard soil sample in Figure 1. The number of samples simultaneously digested is dependent on the analyst. The number may range from 1 to the maximum number of vessels that the microwave units magnetron can heat according to the manufacturer's or literature specifications (the number will depend on the power of the unit, the quantity and combination of reagents, and the heat loss from the vessels).

The pressure should peak between 5 and 15 minutes for most samples (Ref. 2, 3, 5). If the pressure exceeds the pressure limits of the vessel, the pressure will be reduced by the relief mechanism of the vessel.

The total decomposition of some components of a matrix may require or the reaction kinetics are dramatically improved with higher reaction temperatures. If microwave digestion systems and/or vessels are capable of achieving higher temperatures and pressures, the minimum digestion time of 9.5 minutes at a temperature of at least 180 ± 5°C is an appropriate

CD-ROM 3052 - 7 Revision 0 alternative. This change will permit the use of pressure systems if the analysis verifies that 180°C is the minimum temperature maintained by these control systems.

- 7.3.6.1 For reactive substances, the heating profile may be altered for safety purposes. The decomposition is primarily controlled by maintaining the reagents at $180 \pm 5^{\circ}$ C for 9.5 minutes, therefore the time it takes to heat the samples to $180 \pm 5^{\circ}$ C is not critical. The samples may be heated at a slower rate to prevent potential uncontrollable exothermic reactions. The time to reach $180 \pm 5^{\circ}$ C may be increased to 10 minutes provided that $180 \pm 5^{\circ}$ C is subsequently maintained for 9.5 minutes. Decomposition profiles are presented in Figures 1 and 2. The extreme difference in pressure is due to the gaseous digestion products.
- 7.3.6.2 Calibration control is applicable in reproducing this method provided the power in watts versus time parameters are determined to reproduce the specifications listed in 7.3.6. The calibration settings will be specific to the quantity and combination of reagents, quantity of vessels, and heat loss characteristics of the vessels (Ref 1). If calibration control is being used, any vessels containing acids for analytical blank purposes are counted as sample vessels and when fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with the same acid mixture to achieve the full complement of vessels. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbed mass in the cavity (Ref. 1). Irradiate each group of vessels using the predetermined calibration settings. (Different vessel types should not be mixed).
- 7.3.6.3 Pressure control for a specific matrix is applicable if instrument conditions are established using temperature control. Because each matrix will have a different reaction profile, performance using temperature control must be developed for every specific matrix type prior to use of the pressure control system.
- 7.3.7 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave system. When the vessels have cooled to near room temperature, determine if the microwave vessels have maintained a seal throughout the digestion. Due to the wide variability of vessel designs, a single procedure is not appropriate. For vessels that are sealed as discrete separate entities, the vessel weight may be taken before and after digestion to evaluate seal integrity. If the weight loss of sample exceeds 1% of the weight of the sample and reagents, then the sample is considered compromised. For vessels with burst disks, a careful visual inspection of the disk may identify compromised vessels. For vessels with resealing pressure relief mechanisms, an auditory or sometimes a physical sign indicates a vessel has vented.
- 7.3.8 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Vent the vessels using the procedure recommended by the vessel manufacturer. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

- 7.3.8.1 Centrifugation: Centrifugation at 2,000 3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.
- 7.3.8.2 Settling: If undissolved material remains such as TiO, or 2 other refractory oxides, allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.
- 7.3.8.3 Filtering: If necessary, the filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.
- 7.3.9 If the hydrofluoric acid concentration is a consideration in the analysis technique such as with ICP methods, boric acid may be added to permit the complexation of fluoride to protect the quartz plasma torch. The amount of acid added may be varied. depending on the equipment and the analysis procedure. If this option is used, alterations in the measurement procedure to adjust for the boric acid and any bias it may cause are necessary. This addition will prevent the measurement of boron as one of the elemental constituents in the sample. Alternatively, a hydrofluoric acid resistant ICP torch may be used and the addition of boric acid would be unnecessary for this analytical configuration. All major manufacturers have hydrofluoric resistant components available for the analysis of solutions containing hydrofluoric acid.

CAUTION: The traditional use of concentrated solutions of boric acid can cause problems by turning the digestion solution cloudy or result in a high salt content solution interfering with some analysis techniques. Dilute solutions of boric acid or other methods of neutralization or reagent elimination are appropriate to avoid problems with HF and the glass sample introduction devices of analytical instrumentation. Gentle heating often serves to clear cloudy solutions. Matrix matching of samples and standards will eliminate viscosity differences.

7.3.10 The removal or reduction of the quantity of the hydrochloric and hydrofluoric acids prior to analysis may be desirable. The chemistry and volatility of the analytes of interest should be considered and evaluated when using this alternative. Evaporation to near dryness in a controlled environment with controlled pure gas and neutralizing and collection of exhaust interactions is an alternative where appropriate. This manipulation may be performed in the microwave system, if the system is capable of this function, or external to the microwave system in more common apparatus(s). This option must be tested and validated to determine analyte retention and loss and should be accompanied by equipment validation possibly using the standard addition method and standard reference materials. This alternative may be used to alter either the acid concentration and/or acid composition. Note: The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2% (v/v) nitric acid concentration is desirable. Examples of analysis performed with and without removal of the hydrofluoric acid are presented in Table 5. Waste minimization techniques should be used to capture reagent fumes. This procedure should be tested and validated in the apparatus and on standards before using on unknown samples.

- 7.3.11 Transfer or decant the sample into volumetric ware and dilute the digest to a known volume. The digest is now ready for analysis for elements of interest using appropriate elemental analysis techniques and/or SW-846 methods.
- 7.3.12 Sample size may be scaled-up from 0.1, 0.25, or 0.5 g to 1.0 g through a series of 0.2g sample size increments. Scale-up can produce different reaction conditions and/or produce increasing gaseous reaction products. Increases in sample size may not require alteration of the acid quantity or combination, but other reagents may be added to permit a more complete decomposition and oxidation of organic and other sample constituents where necessary (such as increasing the HF for the complete destruction of silicates). Each step of the scale-up must demonstrate safe operation before continuing.
- 7.4 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.
- 7.5 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control to follow performance specifications of the method, then the calibration procedure will not be necessary.

7.5.1 Calibration is the normalization and reproduction of a microwave field strength to permit reagent and energy coupling in a predictable and reproducible manner. It balances reagent heating and heat loss from the vessels and is equipment dependent due to the heat retention and loss characteristics of the specific vessel. Available power is evaluated to permit the microwave field output in watts to be transferred from one microwave system to another.

Use of calibration to control this reaction requires balancing output power, coupled energy, and heat loss to reproduce the temperature heating profile in section 7.3.6. The conditions for each acid mixture and each batch containing the same specified number of vessels must be determined individually. Only identical acid mixtures and vessel models and specified numbers of vessels may be used in a given batch.

7.5.2 For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the system. The calibration format required for laboratory microwave systems depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few systems have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.5.4), otherwise, the analyst must use the multiple point calibration method (7.5.3).

- 7.5.3 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in section 7.5.5. This data is clustered about the customary working power ranges. Nonlinearity has been encountered at the upper end of the calibration. If the system's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.
- 7.5.4 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in section 7.5.5. From the 2-point line calculate the power setting corresponding to the required power in watts specified in the procedure. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.5.3. This point should also be used to periodically verify the integrity of the calibration.
- 7.5.5 Equilibrate a large volume of water to room temperature (23 \pm 2 °C). One kg of reagent water is weighed (1,000.0 g + 0.1 g) into a suitably inert polymeric beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 \pm 2 °C measured to \pm 0.05 °C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the system's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to \pm 0.05 °C. Use a new sample for each additional measurement. If the water is reused, both the water and the beaker must have returned to 23 \pm 2 °C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

Where:

P = the apparent power absorbed by the sample in watts $(W, W = \text{joule sec}^{-1})$

K = the conversion factor for thermochemical calories_sec⁻¹ to watts (which equals 4.184)

Cp = the heat capacity, thermal capacity, or specific heat (cal q^{-1} ${}^{\circ}C^{-1}$) of water

m = the mass of the water sample in grams (g) ΔT = the final temperature minus the initial temperature (°C) t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal g °C) the calibration equation simplifies to: -1 -1

 $P = 34.86 \Delta T$

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation should not vary by more than ±5 V. Electronic components in most microwave units are matched to the system's function and output. When any part of the high voltage circuit, power source, or control components in the system have been serviced or replaced, it will be necessary to recheck the system's calibration. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

8.0 QUALITY CONTROL

- 8.1 All quality control data must be maintained and available for reference or inspection for a period determined by all involved parties based on program or project requirements. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidance.
- 8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).
- 8.3 Spiked samples and/or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.
- 8.4 Blank samples should be prepared using the same reagents and quantities used in sample preparation, placed in vessels of the same type, and processed with the samples.

9.0 METHOD PERFORMANCE

- 9.1 Precision: Precision data for Method 3052 are presented in the tables of this method. Tables 1 through 6 provide a summary of total elemental analysis.
- 9.2 The performance criteria are provided as an example in Figure 1. The temperature profile will be within \pm 5 °C of the mean of the temperature profile, but the pressure curve will vary depending on the acid mixture and gaseous digestion products and the thermal insulating properties of the vessel. Figure 2 provides criteria for the digestion of an oil sample.

10.0 REFERENCES

- 1. Introduction to Microwave Sample Preparation: Theory and Practice, Kingston, H. M. and Jassie, L. B., Eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1988.
- 2. Kingston, H. M., Walter, P. J., Comparison of Microwave Versus Conventional Dissolution for Environmental Applications, Spectroscopy, Vol. 7 No. 9,20-27,1992.
- 3. Kingston, H. M., Haswell, S, Microwave Enhanced Chemistry, ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1997.
- 4. Kingston, H. M.; Walter, P. J.; Lorentzen, E. M. L.; Lusnak, G. P. Report to NIST Office of Standard Reference Materials, The Performance of Leaching Studies on Soil SRMs 2710 and 2711, Duquesne University, Pittsburgh, PA, 1994.
- 5. Kingston, H. M. EPA IAG #DWI-393254-01-0 January 1-March 31, 1988, quarterly Report.
- 6. Kingston, H. M. and Jassie, L. B., "Safety Guidelines for Microwave Systems in the Analytical Laboratory". In Introduction to Microwave Acid Decomposition: Theory and Practice; Kingston, H. M. and Jassie, L. B., eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1988.
- 7. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM, Philadelphia, PA, 1985, D1193-77.
- 8. Kingston, H. M.; Walter, P. J.; Link, D. D. Validation Study and Unpublished Data, Duquesne University, Pittsburgh, PA, 1995. FIGURE 1. TYPICAL REACTION PROFILE FOR THE DIGESTION OF A SOIL (REF. 4 AND 8)

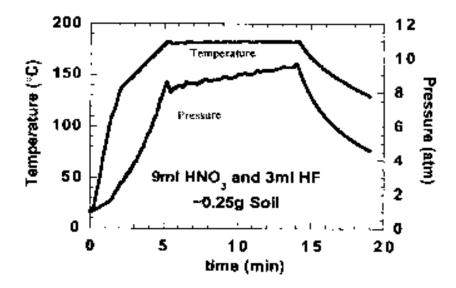


FIGURE 1. TYPICAL REACTION PROFILE FOR THE DIGESTION OF A SOIL (REF. 4 AND 8).

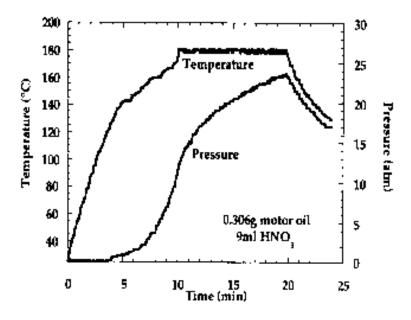


FIGURE 2. TYPICAL REACTION PROFILE FOR THE DIGESTION OF AN OIL (REF. 8)

TABLE 1
ANALYSIS OF NIST SRM 2704 (COMPILATION OF REES IZ AND 3)*
BUFFALO RIVER SEDIMENT

Elément	Analyzed (µg/g)	Certified (µg/g)
Arsenic (n=4)	23.4 ± 2.6	23.4 ± 0.8
Cadmium (n=6)	3.5 + 1.2	3.45 ± 0.22
Chromium (n=6)	1329±13	135 ± 5
Copper (n=6)	98.0 ± 4 2	98.6 ± 5.0
Lead (n=6)	155 ± 9.2	161 ± 17
Mercury (n=4)	1.49 ± 0.14	1.44 ± 0.07
Nickel (n=6)	43.6 ± 3.9	44.1 ± 3.0
Phosphorus (n=4)	1.016 ± 0.016 mg/g	0.998 ± 0.028 mg/g
Selenium (n=4)	1.13 ± 0.9	(1.1)
Sulfor (n=4)	3.56 ± 0.16	
I hallium (n=4)	1 15 ± 0.22	1.2 ± 0.2
Uranium (n=4)	2 97 ± 0.04	3.13 ± 0.13
Zinc (n=6)	441.9 <u>±</u> D.B	438 ± 12

Digestion with 9 mL HNO, and 4 mL HF. Temperature and pressure conditions are as described in Section 7 3.6 of this method and similar to Figure 1. Data reported with 95%.

TABLE 2
ANALYSIS OF NIST SRM 2710 (REFS. 4 AND 3)*
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6).

Elément	Analyzed (µg/g)	Certified (µg/g)
Antimony	39.3 ± 0.9 ⁶	38.4 ± 3.0
Cadmium	21.9 ± 0.7^{-7}	21.B ± 0.2
Chromium	34 0 ± 3.2	(39)
Соррег	2902 ± 83 °	2950 ± 130
Lead	5425 ± 251 ^a	5532 ± 80
Nickel	13.5 ± 1.0 ⁸	14.3 ± 1 0
Silver	36.6 ± 0.5 ⁵	35.3 ± 1.5
Zinc	7007 ± 111°	6952 ± 91

Digestion with either at 9 mL HNO3 and 4 mL HF or b. 9 mL HNO3, 3 mL HF, & 2 mL HCI. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 3
NIST SRM 2711 (REFS. 4 AND 3)
MONTANA SOIL: MODERATELY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6)

Element	Analyzed (µg/g)	Certified (µg/g)
Cadmium	40.5 ± 1.0	41.70 ± 0.25
Chromium	45.5 ± 1.0	(47)
Соррег	106.8 ± 3.4	*14 ± 2
Lead	1161 ± 49	1162 ± 31
Nickel	19.6 ± 0.9	20 6 ± 1 1
Silver	4.3 ± 1.0	4.63 ± 0.39
Zinç	342 ± 9.4	350.4 ± 4.8

Digestion with 9 mL HNO₃ and 4 mL HF. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 4
STABILIZATION AND RECOVERY OF ELEMENTS WITH HCI (REF. 3)* NIST SRM 2/10
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6)

Element	HNO, & HF (µg/g)	HNO ₃ , HF & HCI (µg/g)	Certified (µg/g)
Antimony	33.1 ± 2.1	39.3 ± 0.9	38 4 ± 3.0
Silver	706±45	36.6 ± 0.5	35.3 ± 1.5

¹ HNO, and HF - Digestion used 9 mL and 3 mt, respectively HNO, HF, and HCL - Digestion used 9 mL, 3 mt, and 2 mL respectively. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1 Data reported with 95% confidence intervals.

TABLE 5
FUMING OFF HYDROFLUORIC ACID WITH MICROWAVE EVAPORATION SYSTEM (REF 3)*
MONTANA SOIL, HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=4)

Element	Direct (µg/g)	Fumed (µg/g)	Certified (µg/g)
Antimony	39.3 ± 0.9	39.4 ± 0.9	38 4 ± 3.0
Cadmium	21.9 ± 0.7	23.3 ± 1.6	21.8 ± 0.2
Chramium	340±32	32.4 ± 0.4	(39)
Соррег	2902 ± 83	2870 ± 150	2950 ± 130
Lead	5425 ± 25?	5502 ± 1 06	5532 ± 80
Nickel	13.5 ± 1 0	13.5 ± 0.8	14.3 ± 1.0
Silver	36.6 + 0.5	38.9 ± 1.1	35.3 ± 1.5
Zinc	/007 ± 117	3992 ± 132	6952 + 91

Direct - Digestion used 9 mL HNO₃ and 3 mL HCl or 9 mL HNO₄, 3 mL HF, and 2 mL HCl Furned - Digestion used 9 mL HNO₃ and 3 mL HCl followed by the removal of the FIF. Temperature and pressure conditions are as described in 7.3.6 of the method and similar to Figure 1. The digest solution was furned in a microwave system under vacuum to ~1 mL and 3 mL HCl added. The digest solution was furned to ~1 mL and 3 mL HNO₃ was added. The solution was furned for a final step to ~1 mL and quantitatively transferred and diluted to final volume. Data reported with 95% confidence intervals.

TABLE 6 ANALYSIS OF NIST SRM 1084A (REF. 8) * WEAR METALS IN OIL (100 ppm) (n=4)

Element	Analyzed (µg/g)	Certified (µg/g)	
Chromium	98.1 ± 1.1	98.3 ± 0.8	
Copper	1.2.4 ± 2.4	100.0 ± 1.9	
Lead	99.2 ± 2 3	101 f ± 1.3	
Nickel	99.2 ± 2 4	99.7 ± 1.6	
Silver	102.7 ± 2.2	101 4 ± 1.5	

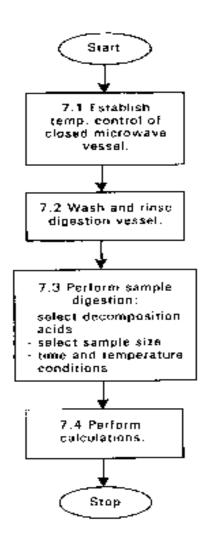
Digestion with 9 mL HNO, and 0.5 mL HF. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 2. Data reported with 95% confidence intervals.

TABLE 7
DIGESTION PARAMETERS USED IN THE ANALYSIS OF SEVERAL MATRICES BY METHOD 3025

Matrix	HNO ₃	HF	HCL
Soil			
NIST SRM 2710 Highly Contaminated Montana Soil	9 ml	3 ml	0-2*ml
NIST SRM 2711 Moderately Contaminated Montana Soil	9	9	0-2*
Sediment			
NIST SRM 2704 Buffalo River Sediment	9	3	0-2*
Biological			
NIST SRM 1566a Oyster Tissue	9	0	0
NIST SRM 1577a Bovine Live	9	0	0
Botanical			
NIST SRM 1515 Apple Leaves	9	0	0
NIST SRM 1547 Peach Leaves	9	0	0
NIST SRM 1572 Citrus Leaves	9	0.5	0
Waste Oil			
NIST SRM 1084a Wear-Metals in Lubricating Oil	9	0.5	0-2*

^{*} HCL is added to stabilize elements such as Ag and Sb when they are analyzed.

METHOD 3052 MICROWAVE ASSISTED ACID DIGESTION OF SILICEOUS AND ORGANICALLY BASED MATRICES



METHOD 6010B

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

1.0 SCOPE AND APPLICATION

- 1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Refer to Chapter Three for the appropriate digestion procedures.
- 1.2 Table 1 lists the elements for which this method is applicable. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the recommended analytical wavelengths and estimated instrumental detection limits for the elements in clean aqueous matrices. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices. Elements and matrices other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest (see Section 8.0) is demonstrated.
- 1.3 Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.
- 1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

2.0 SUMMARY OF METHOD

- 2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Chapter Three). When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.
- 2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background.

intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Section 8.5. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed. 3.0 INTERFERENCES

- Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.
 - 3.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.
 - 3.1.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.
 - 3.1.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction require the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement

CD-ROM 6010B - 2 Revision 2 correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 2. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

- 3.1.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary.
- 3.1.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.
- 3.1.6 The interference effects must be evaluated for each individual instrumen whether configured as a sequential or simultaneous instrument. For each instrument intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 2) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routing for automatic correction on all analyses.
- 3.1.7 Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

- 3.1.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.
- 3.1.9 When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within the 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standard solution should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.
 - 3.1.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.
 - 3.1.10.1 One method is to use a computer software routine for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e., greater than) the analyte instrument detection limit, or false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).
 - 3.1.10.2 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is \geq 20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.
- 3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate

and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance; this may be accomplished with the use of mass flow controllers. The test described in Section 8.5.1 will help determine if a physical interference is present.

- 3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.
- 3.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.
 - 3.5 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.
 - 3.6 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

4.0 APPARATUS AND MATERIALS

- 4.1 Inductively coupled argon plasma emission spectrometer:
 - 4.1.1 Computer-controlled emission spectrometer with background correction.
 - 4.1.2 Radio-frequency generator compliant with FCC regulations.

- 4.1.3 Optional mass flow controller for argon nebulizer gas supply.
- 4.1.4 Optional peristaltic pump.
- 4.1.5 Optional Autosampler.
- 4.1.6 Argon gas supply high purity.
- 4.2 Volumetric flasks of suitable precision and accuracy.
- 4.3 Volumetric pipets of suitable precision and accuracy.

5.0 REAGENTS

- 5.1 Reagent or trace metals grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration of the contamination is less than the MDL then the reagent is acceptable.
 - 5.1.1 Hydrochloric acid (conc), HCl.
 - 5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriately sized beaker.
 - 5.1.3 Nitric acid (conc), HNO₃.
 - 5.1.4 Nitric acid (1:1), HNO₃. Add 500 mL concentrated HNO₃ to 400 mL water and dilute to 1 liter in an appropriately sized beaker.
 - 5.2 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.
 - 5.3 Standard stock solutions may be purchased or prepared from ultra- high purity grade chemicals or metals (99.99% pure or greater). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

Note: This section does not apply when analyzing samples that have been prepared by Method 3040.

<u>CAUTION</u>: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the element fraction and the weight of the metal salt added.

For metals:

For metal salts:

5.3.1 Aluminum solution, stock, 1 mL = 1000 μ g Al: Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1:1) HCl and 1.0 mL of concentrated HN0 $_3$ in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1-liter flask, add an additional 10.0 mL of (1:1) HCl and dilute to volume with reagent water.

NOTE: Weight of analyte is expressed to four significant figures for consistency with the weights below because rounding to two decimal places can contribute up to 4 % error for some of the compounds.

- 5.3.2 Antimony solution, stock, 1 mL = 1000 μ g Sb: Dissolve 2.6673 g K(SbO)C₄H₄O₆ (element fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.3 Arsenic solution, stock, 1 mL = 1000 μ g As: Dissolve 1.3203 g of As₂O₃ (element fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 1.5163 g BaCl₂ (element fraction Ba = 0.6595), dried at 250°C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.5 Beryllium solution, stock, 1 mL = 1000 μ g Be: Do not dry. Dissolve 19.6463 g BeSO₄4H₂O (element fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated HNO₃, and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.6 Boron solution, stock, 1 mL = 1000 μg B: Do not dry. Dissolve 5.716 g anhydrous H₃BO₃ (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1-L volumetric flask with reagent water. Transfer immediately after mixing in a clean polytetrafluoroethylene (PTFE) bottle to minimize any leaching of boron from the glass volumetric container. Use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.
- 5.3.7 Cadmium solution, stock, 1 mL = 1000 μg Cd: Dissolve 1.1423 g CdO (element fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a

minimum amount of (1:1) HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.

- 5.3.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.4969 a CaCO₄ (element Ca fraction = 0.4005), dried at 180°C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_s. Add 10.0 mL concentrated HNO_s and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.9 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.9231 g CrO₃ (element fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO3 and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.10 Cobalt solution, stock, 1 mL = 1000 µg Co: Dissolve 1.00 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO₃. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.11 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.2564 g CuO (element fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO₃. Add 10.0 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.12 Iron solution, stock, 1 mL = 1000 μg Fe: Dissolve 1.4298 g Fe₂O₃ (element fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO₃. Cool, add an additional 5.0 mL of concentrated HNO., and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.13 Lead solution, stock, 1 mL = 1000 μg Pb: Dissolve 1.5985 g Pb(NO₃)₂ (element fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO₃. Add 10 mL (1:1) HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.14 Lithium solution, stock, 1 mL = 1000 µg Li: Dissolve 5.3248 g lithium carbonate (element fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.15 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 1.6584 g MgO (element fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO₃. Add 10.0 mL (1:1) concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.16 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 1.00 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO₃) and dilute to volume in a 1,000 mL volumetric flask with water.

- 5.3.17 Mercury solution, stock, 1 mL = 1000 μ g Hg: Do not dry, highly toxic element. Dissolve 1.354 g HgCl₂ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated HNO₃ and dilute to volume in 1-L volumetric flask with reagent water.
- 5.3.18 Molybdenum solution, stock, 1 mL = 1000 µg Mo: Dissolve 1.7325 g (NH₄)₆Mo₇O₂₄.4H₂O (element fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.19 Nickel solution, stock, 1 mL = 1000 μg Ni: Dissolve 1.00 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO₃, cool, and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.20 Phosphate solution, stock, 1 mL = 1000 μg P: Dissolve 4.3937 g anhydrous KH₂PO₄ (element fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.21 Potassium solution, stock, 1 mL = $1000 \,\mu g$ K: Dissolve 1.9069 g KCi (element fraction K = 0.5244) dried at $110 \,^{\circ}$ C, weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.22 Selenium solution, stock, 1 mL = 1000 μ g Se: Do not dry. Dissolve 1.6332 g H₂SeO₃ (element fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.23 Silica solution, stock, 1 mL = $1000 \mu g$ SiO₂: Do not dry. Dissolve 2.964 g NH₄SiF₆, weighed accurately to at least four significant figures, in 200 mL (1:20) HCl with heating at 85°C to effect dissolution. Let solution cool and dilute to volume in a 1-L volumetric flask with reagent water.
- 5.3.24 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 1.5748 g AgNO₃ (element fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO₃. Dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.25 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 2.5419 g NaCl (element fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.26 Strontium solution, stock, 1 mL = 1000 μg Sr: Dissolve 2.4154 g of strontium nitrate (Sr(NO₃)₂) (element fraction Sr = 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.
- 5.3.27 Thallium solution, stock, 1 mL = 1000 μg TI: Dissolve 1.3034 g TINO₃ (element fraction TI = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.

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- 5.3.28 Tin solution, stock, 1 mL = $1000 \,\mu g$ Sn: Dissolve $1.000 \,g$ Sn shot, weighed accurately to at least 4 significant figures, in $200 \,m$ L (1:1) HCl with heating to effect dissolution. Let solution cool and dilute with (1:1) HCl in a 1-L volumetric flask.
- 5.3.29 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 2.2957 g NH₄VO₃ (element fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.
- $5.3.30\,$ Zinc solution, stock, 1 mL = 1000 μ g Zn: Dissolve 1.2447 g ZnO (element fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO₃. Add 10.0 mL concentrated HNO₃ and dilute to volume in a 1,000 mL volumetric flask with water.
- 5.4 Mixed calibration standard solutions Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Some typical calibration standard combinations are listed in Table 3.
 - NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCI.
- 5.5 Two types of blanks are required for the analysis for samples prepared by any method other than 3040. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample processing.
 - 5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial and continuing calibration blank determinations (see Sections 7.3 and 7.4).
 - 5.5.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

- 5.6 The Initial Calibration Verification (ICV) is prepared by the analyst by combining compatible elements from a standard source different than that of the calibration standard and at concentrations within the linear working range of the instrument (see Section 8.6.1 for use).
- 5.7 The Continuing Calibration Verification (CCV)) should be prepared in the same acid matrix using the same standards used for calibration at a concentration near the mid-point of the calibration curve (see Section 8.6.1 for use).
- 5.8 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number. this spiking procedure will not be necessary.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1 through 3.3.

7.0 PROCEDURE

- 7.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Solubilization and digestion procedures are presented in Sample Preparation Methods (Chapter Three, Inorganic Analytes).
- 7.2 Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer.
 - 7.2.1 Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user or auditor.
 - 7.2.2 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for

a task. Operating conditions for aqueous solutions usually vary from 1100 to 1200 watts forward power, 14 to 18 mm viewing height, 15 to 19 liters/min argon coolant flow, 0.6 to 1.5 L/min argon nebulizer flow, 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. For an axial plasma, the conditions will usually vary from 1100-1500 watts forward power, 15-19 liters/min argon coolant flow, 0.6-1.5 L/min argon nebulizer flow, 1-1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. Reproduction of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively, by adjusting the argon aerosol flow has been recommended as a way to achieve repeatable interference correction factors.

- 7.2.3 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follow manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.
 - 7.2.3.1 Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 ug/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.
 - 7.2.3.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate; set the peristaltic pump to deliver the rate in a steady even flow.
 - 7.2.3.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure can be used for both horizontal and vertical optimization in the radial mode, but is written for vertical. Aspirate a solution containing 10 ug/L of several selected elements. These elements can be As, Se, TI or Pb as the least sensitive of the elements and most needing to be optimize or others representing analytical judgement (V, Cr, Cu, Li and Mn are also used with success). Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least

sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

- 7.2.3.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits.
- 7.2.3.5 If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different, orifice internal diameter is installed, the plasma and viewing height should be reoptimized.
- 7.2.3.6 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular are discussed in the section on interferences. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within ± one reporting limit from zero. The upper control limit is the analyte instrument detection limit. Once established the entire routine must be periodically verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine should be kept on file. Special cases where continual verification is required are described elsewhere.
- 7.2.3.7 Before daily calibration and after the instrument warmup period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same (< 2% change) from day to day.</p>
- 7.2.4 For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements.
- 7.2.5 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.
 - 7.2.5.1 Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit. Refer to Chapter One for additional guidance on the performance of MDL studies.
 - 7.2.5.2 Determination of limits using reagent water represent a best case situation and do not represent possible matrix effects of real world samples.

- 7.2.5.3 If additional confirmation is desired, reanalyze the seven replicate aliquots on two more non consecutive days and again calculate the method detection limit values for each day. An average of the three values for each analyte may provide for a more appropriate estimate. Successful analysis of samples with added analytes or using method of standard additions can give confidence in the method detection limit values determined in reagent water.
- 7.2.5.4 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum for three, preferably five, different concentration standards across the range. One of these should be near the upper limit of the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. The upper range limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined analyte concentrations that are above the upper range limit must be diluted and reanalyzed. The analyst should also be aware that if an interelement correction from an analyte above the linear range exists, a second analyte where the interelement correction has been applied may be inaccurately reported. New dynamic ranges should be determined whenever there is a significant change in instrument response. For those analytes that periodically approach the upper limit, the range should be checked every six months. For those analytes that are known interferences, and are present at above the linear range, the analyst should ensure that the interelement correction has not been inaccurately applied.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self absorption effects. These curves may be used if the instrument allows; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.995 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and should be checked whenever there have been moderate equipment changes.

- 7.2.6 The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.
- 7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 5.4. Flush the system with the calibration blank (Section 5.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve must consist of a minimum of a blank and a standard.
- 7.4 For all analytes and determinations, the laboratory must analyze an ICV (Section 5.6), a calibration blank (Section 5.5.1), and a continuing calibration verification (CCV) (Section 5.7) immediately following daily calibration. A calibration blank and either a calibration verification (CCV) or an ICV must be analyzed after every tenth sample and at the end of the sample run. Analysis of

the check standard and calibration verification must verify that the instrument is within ± 10% of calibration with relative standard deviation < 5% from replicate (minimum of two) integrations. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICV, CCV or check standard must be reanalyzed. The analysis data of the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

- 7.5 Rinse the system with the calibration blank solution (Section 5.5.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration.
- 7.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported with up to three significant figures.
- 7.7 The MSA should be used if an interference is suspected or a new matrix is encountered. When the method of standard additions is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by: multiplying the intensity value for the unfortified aliquot by the volume (Liters) and concentration (mg/L or mg/kg) of the standard addition to make the numerator; the difference in intensities for the fortified sample and unfortified sample is multiplied by the volume (Liters) of the sample aliquot for the denominator. The quotient is the sample concentration.

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution.

NOTE: Refer to Method 7000 for a more detailed discussion of the MSA.

7.8 An alternative to using the method of standard additions is the internal standard technique. Add one or more elements not in the samples and verified not to cause an interelement spectral interference to the samples, standards and blanks; yttrium or scandium are often used. The concentration should be sufficient for optimum precision but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences especially in high solids matrices.

8.0 QUALITY CONTROL

- 8.1 All quality control data should be maintained and available for easy reference or inspection. All quality control measures described in Chapter One should be followed.
- 8.2 Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

- 8.3 Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water carried through the same preparation process as a sample (refer to Chapter One).
- 8.4 Analyze matrix spiked duplicate samples at a frequency of one per matrix batch. A matrix duplicate sample is a sample brought through the entire sample preparation and analytical process in duplicate.
 - 8.4.1.1 The relative percent difference between spiked matrix duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where:

RPD = relative percent difference.

 $D_1 =$ first sample value.

 $D_2 =$ second sample value (replicate).

(A control limit of \pm 20% RPD or within the documented historical acceptance limits for each matrix shall be used for sample values greater than ten times the instrument detection limit.)

- 8.4.1.2 The spiked sample or spiked duplicate sample recovery is to be within ± 25% of the actual value or within the documented historical acceptance limits for each matrix.
- 8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Sections 8.5.1 and 8.5.2, will ensure that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.
 - 8.5.1 Dilution Test: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected.
 - 8.5.2 Post Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

<u>CAUTION</u>: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

- 8.6 Check the instrument standardization by analyzing appropriate QC samples as follows.
- 8.6.1 Verify calibration with the Continuing Calibration Verification (CCV) Standard immediately following daily calibration, after every ten samples, and at the end of an analytical run. Check calibration with an ICV following the initial calibration (Section 5.6). At the laboratory's discretion, an ICV may be used in lieu of the continuing calibration verifications. If used in this manner, the ICV should be at a concentration near the mid-point of the calibration curve. Use a calibration blank (Section 5.5.1) immediately following daily calibration, after every 10 samples and at the end of the analytical run.
 - 8.6.1.1 The results of the ICV and CCVs are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.
 - 8.6.1.2 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.
 - 8.6.1.3 The results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.
- 8.6.2 Verify the interelement and background correction factors at the beginning of each analytical run. Do this by analyzing the interference check sample (Section 5.8). Results should be within ± 20% of the true value.

9.0 METHOD PERFORMANCE

- 9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.
- 9.2 Performance data for aqueous solutions and solid samples from a multilaboratory study (9) are provided in Tables 5 and 6.

10.0 REFERENCES

- Boumans, P.W.J.M. <u>Line Coincidence Tables for Inductively Coupled Plasma Atomic</u> Emission Spectrometry, 2nd Edition. Pergamon Press, Oxford, United Kingdom, 1984.
- Sampling and Analysis Methods for Hazardous Waste Combustion; U.S. Environmental Protection Agency; Air and Energy Engineering Research Laboratory, Office of Research and Development: Research Triangle Park, NC, 1984; Prepared by Arthur D. Little, Inc.

- 3. Rohrbough, W.G.; et al. <u>Reagent Chemicals. American Chemical Society Specifications</u>, 7th ed.; American Chemical Society: Washington, DC, 1986.
- 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.
- Jones, C.L. et al. <u>An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission</u> Spectroscopy Method 6010 and Digestion Method 3050. EPA-600/4-87-032, U.S. Environmental Protection Agency, Las Vegas, Nevada, 1987.

TABLE 1
RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection	-	Estimated IDL ^b
Element	Wavelength ^a (nm)	(µg/L)
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678x2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194,227x2	17
Molybdenum	202.030	5.3
Nickel	231.604x2	10
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	50
Silica (SiO ₂)	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980x2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856x2	1.2

^aThe wavelengths listed (where x2 indicates second order) are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted (e.g., in the case of an interference) if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 3.1). In time, other elements may be added as more information becomes available and as required.

^bThe estimated instrumental detection limits shown are provided as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

^cHighly dependent on operating conditions and plasma position.

TABLE 2
POTENTIAL INTERFERENCES
ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM
INTERFERENCE AT THE 100-mg/L LEVEL⁰

	Interferant ^{a,b} Wavelength										
Analyte	(nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	٧
Aluminum Antimony Arsenic	308.215 206.833 193.696	0.47 1.3	-	 2.9 0.44	-	0.08		0.21		0.25	1.4 0.45 1.1
Barium Beryllium	455.403 313.042			-		-				0.04	0.05
Cadmium Calcium Chromium Cobalt Copper	226.502 317.933 267.716 228.616 324.754		 	0.08 0.03		0.03 0.01 0.003 0.005 0.003	0.01 	0.04 0.04 	0.02	0.03 0.15 0.05	0.03 0.04 0.02
Iron Lead Magnesium Manganese	259.940 220.353 279.079 257.610	0.17 0.005	 0.02 	 0.11 0.01		 0.13 0.002	 0.002	0.12 0.25 	 	0.07	 0.12
Molybdenum Nickel Selenium Sodium Thallium Vanadium Zinc	202.030 231.604 196.026 588.995 190.864 292.402 213.856	0.05 0.23 0.30		0.05	 0.14	0.03 0.09 0.005			 0.29	 0.08 0.02	

Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

AI -	1000 mg/L	Mg - 1000 mg/l
Ca -	1000 mg/L	Mn - 200 mg/L
Cr -	200 mg/L	Tl - 200 mg/Ľ
Cu -	200 mg/L	V - 200 mg/L
Fe -	1000 mg/L	·

The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

Interferences will be affected by background choice and other interferences may be present.

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TABLE 3 MIXED STANDARD SOLUTIONS

Solution	Elements
ı	Be, Cd, Mn, Pb, Se and Zn
11	Ba, Co, Cu, Fe, and V
H	As, Mo
IV	Al, Ca, Cr, K, Na, Ni,Li, and Sr
V	Ag (see "NOTE" to Section 5.4), Mg, Sb, and TI
VI	P

TABLE 4. ICP PRECISION AND ACCURACY DATA^a

True Mean Conc. (ug/L) (ug/L) (ug/L) 750 733 749 750 749 749 750 208 749 700 696 700 696 700 696 700 700 512		Accuracy ^d								
750 733 350 345 750 749 200 208 150 149 250 235 600 594 700 696 50 48 700 512 700 512	6.2 2.7 1.8 7.5	(%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD	Accuracy ^d (%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD ^b (%)	Accuracy [±] (%)
350 345 750 749 200 208 150 149 250 235 600 594 700 696 50 48 700 512 1 700	1.8	98	20	20	9.8	100	180	176	5.2	86
750 749 200 208 150 149 250 235 600 594 700 696 50 48 700 512 1 700	7.5	66	15	15	6.7	100	100	66	3.3	66
200 208 150 149 250 235 600 594 700 696 50 48 1	7.5	100	70.	69	2.9	66	170	169	1.1	66
150 149 250 235 600 594 700 696 50 48 1 700 512 1	***	104	22	19	23	86	09	63	17	105
250 235 600 594 700 696 50 48 1 700 512 1	3.8	66	10	10	18	100	50	50	3.3	100
600 594 700 696 50 48 1 700 512 1	5.1	94	+	11	40	100	70	67	7.9	96
700 696 50 48 1 700 512 1	3.0	66	20	19	15	95	180	178	6.0	66
50 48 700 512	5.6	66	09	62	33	103	160	161	13	101
700 512	12	96	2.5	2.9	16	116	14	13	16	93
	10	73	20	20	4.1	100	120	108	21	06
Ni 250 245 5.	5.8	86	30	28	Ξ	93	9	55	14	92
Pb 250 236 16	16	94	24	30	32	125	80	80	14	100
Zn 200 201 5.	5.6	100	16	19	45	119	80	82	9.4	102
Se° 40 32 21.	21.9	80	9	8.5	42	142	10	8.5	8.3	. 85

^aNot all elements were analyzed by all laboratories.

CRSD = relative standard deviation.

CRESUITS for Se are from two laboratories.

Accuracy is expressed as the mean concentration divided by the true concentration times 100.

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TABLE 5
ICP-AES PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS®

Element	Mean Conc. (mg/L)	N⁵	RSD ^b (%)	Accuracy ^c (%)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8 7	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Мо	3.70	8	6.9	100
Ni	3.70	7	5.7	. 100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Ag	3.69	6	9.1	100
Na	14.0	8 7	4.2	95
TI	15.1	7	8.5	102
V	3.51	8 8	6.6	95
Zn	3.57	8	8.3	96

athese performance values are independent of sample preparation because the labs analyzed portions of the same solutions

^bN = Number of measurements for mean and relative standard deviation (RSD).

^eAccuracy is expressed as a percentage of the nominal value for each analyte in acidified, multielement solutions.

TABLE 6
ICP-AES PRECISION AND BIAS FOR SOLID WASTE DIGESTS*

	Spiked C				Spiked Electroplating Sludge			
Element	Mean Conc. (mg/L)	N ^b	RSD ^b (%)	Bias° (%AAS)	Mean Conc. (mg/L)	N⁵	RSD ^b (%)	Bias ^c (%AAS)
Al	330	8	16	104	127	8	13	110
Sb	3.4	6	73	96	5.3	7	24	120
As	21	8	83	270	5.2	7	8.6	87
Ba	133	8	8.7	101	1.6	8	20	58
Be	4.0	8	57	460	0.9	7	9.9	110
Cd	0.97	6	5.7	101	2.9	7	9.9	90
Ca	87	6	5.6	208	954	7	7.0	97
Cr	2.1	7	36	106	154	7	7.8	93
Co	1.2	6	21	94	1.0	7	11	85
Cu	1.9	6	9.7	118	156	8 7	7.8	97
Fe	602	8	8.8	102	603	7	5.6	98
Pb	4.6	7	22	94	25	7	5.6	98
Mg	15	8	15	110	35	8	20	84
Mn	1.8	7	14	104	5.9	7	9.6	95
Mo	891	8	19	105	1.4	7	36	110
Ni	1.6	6	8.1	91	9.5	7	9.6	90
K	46	8	4.2	98	51	8	5.8	82
Se	6.4	5	16	73	8.7	7	13	101
Ag	1.4	3	17	140	0.75	7	19	270
Na	20	8	49	130	1380	8	9.8	95
Tì	6.7	4	22	260	5.0	7	20	180
V	1010	5	7.5	100	1.2	6 7	11	80
Zn	2.2	6	7.6	93	266	7	2.5	101

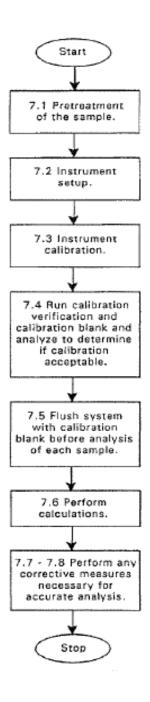
^aThese performance values are independent of sample preparation because the labs analyzed portions of the same digests.

^bN = Number of measurements for mean and relative standard deviation (RSD).

[&]quot;Bias for the ICP-AES data is expressed as a percentage of atomic absorption spectroscopy (AA) data for the same digests.

METHOD 6010B

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY



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METHOD 6020

<u>INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY</u>

1.0 SCOPE AND APPLICATION

- 1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-ug/L concentrations of a large number of elements in water samples and in waste extracts or digests [1,2]. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.
- 1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability of Method 6020 in a multi-laboratory study on solid wastes are listed in Table 1. Acceptability of the method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectroscopy or inductively coupled plasma-atomic emission spectroscopy. It should be noted that the multi-laboratory study was conducted in 1986. Multi-laboratory performance data for the listed elements (and others) are provided in Section 9. Instrument detection limits, sensitivities, and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, detection limits will generally be below 0.02 µg/L.
- 1.3 If Method 6020 is used to determine any analyte not listed in Table 1, it is the responsibility of the analyst to demonstrate the accuracy and precision of the Method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Section 8.4).
- 1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.
- 1.5 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^6Li , ^{45}Sc , ^{89}Y ^{103}Rh , ^{115}In ^{165}Ho , and ^{209}Bi . The lithium internal standard should have an enriched abundance of ^6Li , so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant amounts of the recommended internal standards.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples which require total ("acid-leachable") values must be digested using appropriate sample preparation methods (such as Methods 3005 - 3051).

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2.2 Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 INTERFERENCES

- 3.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isoptope, or use of another method.
- 3.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified i n the literature [3,4] . Examples include ArCl+ ions on the 7s As signal and Moo' ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature [5], the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the 35C1 natural abundance of 75.77 percent is 3.13 times the ³⁷C1 abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the 38Ar37C1+ contribution at m/z 75 is a negligible 0.06 percent of the 40Ar35CI+ signal):

corrected arsenic signal (using natural isotopes abundances for coefficient approximations)=

(m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the)final term adjusts for any selenium contribution at 77 m/z),

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than 82 Se+, (e.g., 81BrH+ from bromine wastes [6]).

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Similarly,

corrected cadmium signal (using natural isotopes abundances for coefficient approximations) =

 $(m/z \ 114 \ signal) - (0.027)(m/z \ 118 \ signal) - (1.63)(m/z \ 108 \ signal), (where last 2 terms adjust for any tin or Moo' contributions at <math>m/z \ 114$).

<u>NOTE:</u> Cadmium values will be biased low by this type of equation when 92 ZrO' ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct (94 ZrOH+) and indirect (90 ZrO+) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients in the Cd equation are ONLY illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found [7] to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferant. This type of correction has been reported [7] for oxide-ion corrections using ThO+/Th+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas have been shown to greatly reduce molecular interferences [8]. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

- 3.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement [9]. Dissolved solids can deposit on the nebul i zer tip of a pneumatic nebul i zer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended [10] to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes [11]. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.
- 3.4 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample

deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

4.0 APPARATUS AND MATERIALS

- 4.1 Inductively coupled plasma-mass spectrometer:
- 4.1.1 A system capable of providing resolution, better than or equal to amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.
 - 4.1.2 Argon gas supply: high-purity grade (99.99%).

5.0 REAGENTS

- 5.1 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 per cent (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used [3,4]. Concentrations of antimony and silver between 50-500 $\mu g/L$ require 1% (v/v) HCl for stability; for concentrations above 500 $\mu g/L$ Ag, additional HCl will be needed.
- 5.2 Reagent water: All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.
- 5.3 Standard stock solutions may be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 or greater purity). See Method 6010A, Section 5.3, for instructions on preparing standard solutions from solids.
 - 5.3.1 Bismuth internal standard solution, stock, $1\text{mL}=100_{ug}$ Bi: Dissolve 0.1115 g Bi $_20_3$ in a minimum amount of dilute HNO $_3$. Add 10mL conc. HNO $_3$ and dilute to 1,000mL with reagent water.
 - 5.3.2 Holmium internal standard solution, stock, 1mL = 100 μ g Ho: Dissolve 0.1757 g $HO_2(CO_3)2.5H_2O$ in 10mL reagent water and 10mL HNO_3 . After dissolution is complete, warm the solution to d egas. Add 10mL conc. HNO_3 and dilute to 1,000mL with reagent water.

- 5.3.3 Indium internal standard solution, stock, $1\text{mL}=100~\mu\text{g}$ In: Dissolve 0.1000~g indium metal in 10mL conc. $\text{HNO}_3.$ Dilute to 1,000mL with reagent water.
- 5.3.4 Lithium internal standard solution, stock, 1mL = 100 jig $^6\text{Li:}$ Dissolve 0.6312 g 95-atom-% ^6Li , Li $_2\text{CO}_3$ in 10mL of reagent water and 10mL HNO $_3$. After dissolution is complete, warm the solution to degas. Add 10mL conc. HNO $_3$ and dilute to 1,000mL with reagent water.
- 5.3.5 Rhodium internal standard solution, stock, 1mL=100 jig Rh: Dissolve 0.3593 g ammonium hexachlororhodate (III) $(\text{NH}_4)_3\text{RhCl}_6$ in 10mL reagent water. Add 100mL conc. HCl and dilute to 1,000mL with reagent water.
- 5.3.6 Scandium internal standard solution, stock, $1\text{mL}=100~\mu g$ Sc: Dissolve 0.15343~g Sc_2O_3 in 10mL (1+1) hot $\text{HNO}_3.$ Add 5mL conc. HNO_3 and dilute to 1,000mL with reagent water.
- 5.3.7 Terbium internal standard solution, stock, 1mL=100 jig Tb: Dissolve 0.1828 g $\text{Tb}_2(\text{CO}_3)_3\cdot~5\text{H}_2\text{O}$ i n 10mL (1+1) HNO3. After dissolution is complete, warm the solution to degas. Add 5mL conc. HNO3 and dilute to 1,000mL with reagent water.
- 5.3.8 Yttrium internal standard solution, stock, 1mL = 100 jig Y: Dissolve 0.2316 g $Y_2(C0_3)_3.3H_2O$ in 10mL (1+1) HNO₃. Add 5mL conc. HNO sand dilute to 1,000mL with reagent water.
- 5.3.9 Titanium solution, stock, 1mL = 100 μg Ti: Dissolve 0.4133 g (NH₄)₂TiF₆ in reagent water. Add 2 drops conc. HF and dilute to 1,000mL with reagent water.
- 5.3.10 Molybdenum solution, stock, $1mL = 100_{ug}$ Mo: Dissolve 0.2043 g (NH₄)₂MoO₄ in reagent water. Dilute to 1,000mL with reagent water.
- 5.4 Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1 percent (v/v) HNO3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold.) Generally, an internal standard should be no more than 50amu removed from the analyte. Recommended internal standards include ⁶Li, ⁴⁵Sc, ⁸⁹Y, ¹⁰³Rh, ¹⁵In, ¹⁵⁹Th, ¹⁶⁹ Ho, and ²⁰⁹ Bi. Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standards solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard (see Section 5.7) and monitored weekly for stability.
- 5.5 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The preparation blank is used to monitor for possible contamination resulting from

the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

- 5.5.1 The calibration blank consists of the same concentration(s) of the same acids) used to prepare the final dilution of the calibrating solutions of the analytes [often 1 percent \mbox{HNO}_3 (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes. Use of HCl for antimony and silver is cited in Section 5.1
- 5.5.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.
- 5.5.3 The rinse blank consists of 1 to 2 percent HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.
 - NOTE: The ICS solutions in Table 2 are intended to evaluate corrections for known interferences on only the analytes in Table 1. If Method 6020 is used to determine an element not listed in Table 1, it is the responsibility of the analyst to modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see section 8.4).
- 5.6 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}\text{Cl}^{160}$ + on 51 V+ and $^{40}\text{Ar}^{35}\text{Cl}^{+}$ on $^{75}\text{As}^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.
 - 5.6.1 These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.
 - 5.6.1.1 Mixed ICS solution I may be prepared by adding 13.903g Al $(\text{NO}_3)_3\cdot 9\text{H}_2\text{O},~2.498g$ CaCO $_3$ (dried at 180 C for 1 h before weighing), 1.000g Fe, 1.658g MgO, 2.305g Na $_2\text{CO}_3$, and 1.767g K $_2\text{CO}_3$ to 25mL of reagent water. Slowly add 40mL of (1+1) HNO $_3$. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000mL with reagent water.
 - 5.6.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g 85 % $H_3PO_4,\ 6.373$ g 96% $H_2SO_4,\ 40.024$ g 37% HCl, and 10.664 g citric acid C_6O,H_8 to 100mL of reagent water. Dilute to 1,000mL with reagent water.
 - 5.6.1.3 Mixed ICS solution III may be prepared by adding 1.00mL each of 100-µg/mL arsenic, cadmium, chromium, cobalt, copper, manganese, nickel, silver, and zinc stock solutions to about

50 mL reagent water. Add 2.0 mL concentrated $\text{HNO}_3,$ and dilute to 100.0 mL with reagent water.

5.6.1.4 Working ICS Solutions

- 5.6.1.4.1 ICS-A may be prepared by adding 10.0 mL of mixed ICS solution I (5.7.1.1), 2.0 mL each of 100 ug/mL titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), and 5.0 mL of mixed ICS solution II (5.7.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.
- 5.6.1.4.2 ICS-AB may be prepared by adding 10.0 mL of mixed ICS solution I $(5.7.1.1),\ 2.0 mL$ each of $100 \mu g/mL$ titanium stock solution (5.3.9) and molybdenum stock solution $(5.3.10),\ 5.0 mL$ of mixed ICS solution II $(5.7.1.2),\ and\ 2.0 mL$ of Mixed ICS solution III (5.7.1.3). Dilute to 100 mL with reagent water. Although the ICS solution AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly.
- 5.7 The quality control standard is the initial calibration verification solution (ICV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration.
- 5.8 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest (for example, 10 $_{\mu g/L}$ of Li, Co, In, and T1) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 7.5). This solution is also used to verify that the instrument has reached thermal stability (See Section 7.4).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 Sample collection procedures should address the considerations described in Chapter Nine of this Manual.
- 6.2 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1.3 for information on sample handling and preservation. Only polyethylene or fluorocarbon (TFE or PFA) containers are recommended for use in Method 6020.

7.0 PROCEDURE

- 7.1 Solubilization and digestion procedures are presented in the Sample Preparation Methods (e.g., Methods 3005 3051).
- 7.2 Initiate appropriate operating configuration of the instruments computer according to the instrument manufacturer's instructions.
- 7.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

- 7.4 Operating conditions: The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (Section 5.8) at least four times with relative standard deviations of \leq 5% for the analytes contained in the tuning solution.
 - NOTE: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.
- 7.5 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9amu full width at 10 percent peak height.
- 7.6 Calibrate the instrument for the analytes of interest (recommended isotopes for the analytes in Table 1 are provided in Table 3), using the calibration blank and at least a single initial calibration standard according to the instrument manufacturer's procedure. Flush the system with the rinse blank (5.5.3) between each standard solution. Use the average of at leastthree integrations for both calibration and sample analyses.
- 7.7 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are liste in Table 3.
- 7.8 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the calibration verification solution (Section 5.7). When measurements exceed \pm 10% of the accepted value, the analyses must be terminated, the problem corrected, the instrument recalibrated, and the new calibration verified. Any samples analyzed under an out-of-control calibration must be reanalyzed. During the course of an analytical run, the instrument may be "resloped" or recalibrated to correct for instrument drift. A recalibration must then be followed immediately by a new analysis of a CCV and CCB before any further samples may be analyzed.
- 7.9 Flush the system with the rinse blank solution (5.5.3) until the signal levels return to the method's levels of quantitation (usually about 30 seconds) before the analysis of each sample (see Section 7.7). Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (Section 5.6) and the calibration blank (Section 5.5.1) at a frequency of at least once every 10 analytical samples. Flow-injection systems may be used as long as they can meet the performance criteria of this method.
- 7.10 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 7.6 and 7.8).

- 7.11 Calculations: The quantitative values shall be reported in appropriate units, such as micrograms per liter(ug/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values.
 - 7.11.1 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:
 - (1) A separate determination of percent solids must be performed.
 - (2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

Concentration (dry weight)(mg/kg) = (CXV)/(WxS) Where.

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation

W = Weight in kg of wet sample

S = % Solids/100

Calculations should include appropriate interference corrections (see Section 3.2 for examples), internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

8.0 QUALITY CONTROL

- $8.1\,$ All quality control data should be maintained and be available for easy reference or inspection.
- 8.2 Instrument Detection Limits (IDLs) in $_{ug/L}$ can be estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months and kept with the instrument log book. Refer to Chapter One for additional guidance.
- 8.3 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the initial calibration standard, the following procedure is followed. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal standard intensities fall within the prescribed window. The intensity levels of the internal standards for the calibration blank (Section 5.5.1) and instrument check standard (Section 5.6) must agree within \pm 20 percent of the intensity level of the internal standard of the original calibration solution. If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

8.4 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use the observed isotopic-response ratios or parent-tooxide ratios (provided an oxide internal standard is used as described in Section 3.2) for each instrument system are acceptable corrections for use in Method 6020.

- 8.5 Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, refer to Section 5.5.2), an analysis of a fivefold (1+4) dilution must agree within \pm 10% of the original determination. If not, an interference effect must be suspected. One dilution test must be included for each twenty samples (or less) of each matrix in a batch.
- 8.6 Post-Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect (Refer to Method 7000).
- $8.7\,$ A Laboratory Control Sample (LCS) should be analyzed for each analyte using the same sample preparations, analytical methods and OA/QC procedures employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less.
- 8.8 Check the instrument calibration by analyzing appropriate quality control solutions as follows:
 - 8.8.1 Check instrument calibration using a calibration blank (Section 5.5.1) and the initial calibration verification solution (Sections 5.7 and 7.9).

- 8.8.2 Verify calibration at a frequency of every 10 analytical samples with the instrument check standard (Section 5.6) and the calibration blank (Section 5.5.1). These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last
- 8.8.3 The results of the initial calibration verification solution and the instrument check standard must agree within $\pm~10\%$ of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed.
- 8.8.4 The results of the calibration blank must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed. If the laboratory consistently has concentrations greater than 3 times the IDL, the IDL may be indicative of an estimated IDL and should be re-evaluated.
- 8.9 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. Refer to Section 3.0 for a discussion on intereferences and potential solutions to those intereferences if additional guidance is needed.
- Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.
 - The relative percent difference (RPD) between duplicate 8.10.1 determinations must be calculated as follows:

RPD =
$$\frac{|ID, -D_z|}{(D_1 + D_2)/2} \times 100$$

where:

RPD = relative percent difference. D_1 = first sample value.

 D_2 = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition must be reanalyzed.

9.0 METHOD PERFORMANCE

9.1 In an EPA multi-laboratory study, 10 laboratories applied the ICP-MS technique to both aqueous and solid samples. TABLE 4 summarizes the method performance data for aqueous samples. Performance data for solid samples is provided in TABLE 5.

10.0 REFERENCES

- 1. Horlick, G., et al., Spectrochim. Acta 40B, 1555 (1985).
- 2. Gray, A.L., Spectrochim. Acta 40B, 1525 (1985); 41B, 151 (1986).
- 3. Tan, S.H., and Horlick, G., Appl. Spectrosc. 40, 445 (1986). 4.

Vaughan, M.A., and Horlick, G., Appl. Spectrosc. 40, 434 (1986).

- 5. Holden, N.E., "Table of the Isotopes," in Lide, D.R., Ed., CRC Handbook of Chemistry and Physics, 74th Ed., CRC Press, Boca Raton, FL, 1993.
- 6. Hinners, T.A., Heithmar, E., Rissmann, E., and Smith, D., Winter Conference on Plasma Spectrochemistry, Abstract THP18; p. 237, San Diego, CA (1994).
- 7. Lichte, F.[., et al., Anal. Chem. 59, 1150 (1987).
- 8. Evans E.H., and Ebdon, L., J. Anal. At. Spectrom. 4, 299 (1989).
- 9. Beauchemin, D., et al., Spectrochim. Acta 42B, 467 (1987). 10.

Houk, R.S., Anal. Chem. 58, 97A (1986).

11. Thompson, J.J., and Houk, R.S., Appl. Spectrosc. 41, 801 (1987).

TABLE 1. ELEMENTS APPROVED FOR ICP-MS DETERMINATION

Element	CAS* #
Aluminum Antimony Arsenic Barium Bervllium Cadmium Chromium Cobalt Copper Lead Manganese Nickel Silver Thallium Zinc	7429-90-5 7440-36-0 7440-38-2 7440-39-3 7440-41-7 7440-43-9 7440-47-3 7440-48-4 7440-50-8 7439-92-1 7439-96-5 7440-02-0 7440-22-4 7440-28-0 7440-66-6

TABLE 2. RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

Solution component	Solution A Concentration(mg/L)	Solution AB Concentration (mg/L)
Al Ca Fe Ma Na P K S C C Mo Ti AC C C O Mn Aq Na Zn	100.0 100.0 100.0 100.0 100.0 100.0 100.0 200.0 1000.0 2.0 2.0 0.0 0.0 0.0 0.0 0.0	100.0 100.0 100.0 100.0 100.0 100.0 100.0 200.0 1000.0 2.0 2.0 0.0200 0.0200 0.0200 0.0200 0.0200 0.0200 0.0200 0.0200 0.0200 0.0200 0.0200 0.0200 0.0200 0.0200 0.0200

TABLE 3. RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Mass	Element of interest
27 121 123 75 138 137, 136, 135, 134 9 209 114 112, 111, 110, 113, 42, 43, 44, 46, 48 35, 37, (77, 82)a 59 63, 65 165 115 113 56, 54, 57, 58 139 208 207, 206, 204 6 ^b 7 24, 25, 26 98, 96, 92, 97, (108)a 58, 60, 62, 61, 64 39 103 45 107 109 23 159 205 203 120 118	Aluminum Antimonv Arsenic Barium Beryllium Bismuth (IS) Cadmium Calcium (I) Chlorine (I) Chromium Cobalt Copper Holmium (IS) Indium (IS) Iron (I) Lanthanum (I) Lead Lithium (IS) Magnesium (I) Manganese Molybdenum (I) Nickel Potassium (I) Rhodium (IS) Scandium (IS) Scandium (IS) Scilver Sodium (I) Terbium (IS) Thallium Tin (I)
89 64,66,68, 67,70	Yttrium (IS) Zinc

NOTE: Method 6020 is recommended for only those analytes listed in Table 1. Other elements are included in this table because they are potential interferent (labeled 1) in the determination of recommended analytes, or they are commonly used internal standarda (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes. a These masses are also useful for interference correction (Section 3.2). b Internal standard must be enriched in the isotope. This minimizes interference from indigenous lithium.

TABLE 4. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparabilityª Range	%RSD Range	N ^b	S ^c
Aluminum Antimony Arsenic Barium Beryllium Cadmium Calcium Chromium Cobalt Copper Iron Lead Magnesium Manganese Nickel Potassium Selenium Silver Sodium Thallium Vanadium Zinc	95 - 100 97 - 114 91 - 99 103 - 107 98 - 102 99 - 107 95 - 105 101 - 104 85 - 101 91 - 900 71 - 137 98 - 102 95 - 101 98 - 101 101 - 114 102 - 107 104 - 105 82 - 104 88 - 97 107 - 142 93 - 102	11 - 14 5 7.6 7 48 4 9.0 8 14 4 7.2 5 27 8 8.5 6 27 11 - 150 11 - 23 10 - 15 8 15 6 6.7 9 19 15 - 25 5 7.7 24 - 43 9 12 23 - 68 6 17	1 - 14 1 - 16 1 - 14 1 - 18 1 - 18	4345335435565425325335

 $^{^{\}mbox{\tiny a}}$ Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique.

 $^{^{\}rm b}$ N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value).

 $^{^{\}rm c}$ S is the number of samples with results greater than the limit of quantitation.

 $^{^{\}rm d}$ No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

TABLE 5. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

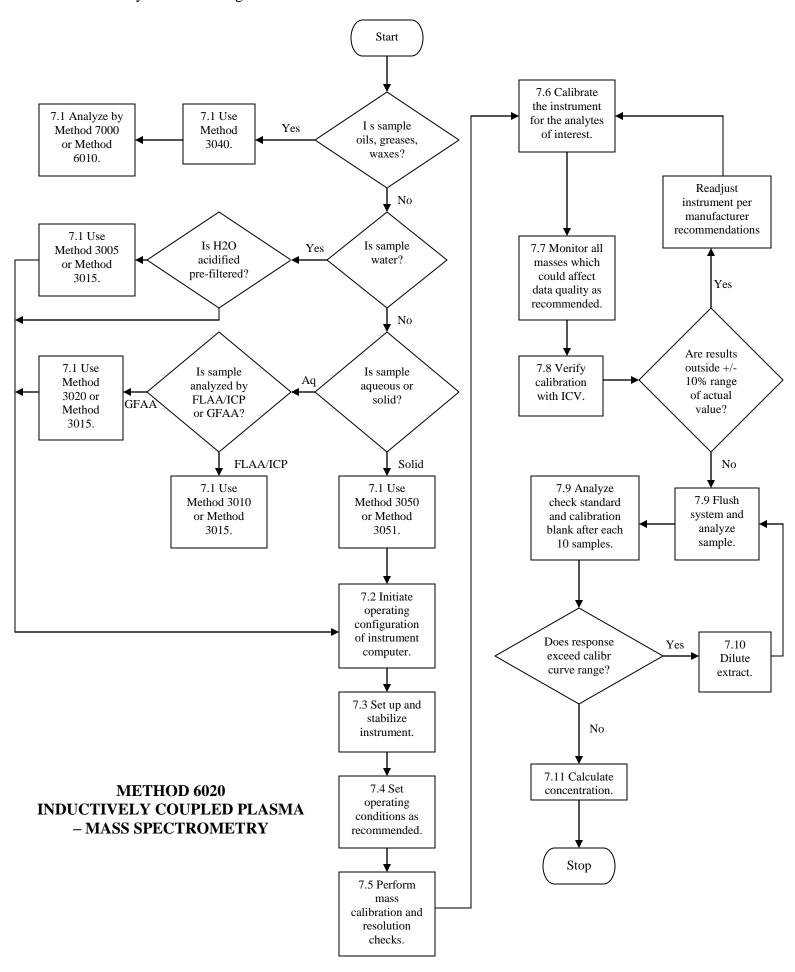
Element	Comparability ^a Range	%RSD Range	N_p	S ^c
Aluminum Antimonv Arsenic Barium Bervllium Cadmium Calcium Chromium Cobalt Copper Iron Lead Magnesium Manganese Nickel Potassium Selenium Silver Sodium Thallium Vanadium Zinc	83 - 101 D 79 - 102 100 - 102 50 - 87 93 - 100 95 - 109 77 - 98 43 - 102 90 - 109 87 - 99 90 - 104 89 - 111 80 - 108 87 - 117 97 - 137 81 43 - 112 100 - 146 91 83 - 147 84 - 124	11 - 39 12 - 21 12 - 23 4.3 - 17 19 - 34 6.2 - 25 4.1 - 27 11 - 32 15 - 30 9.0 - 25 6.7 - 21 5.9 - 28 7.6 - 37 11 - 40 9.2 - 29 11 - 62 39 12 - 33 14 - 77 33 20 - 70 14 - 42	13 - 14 15 - 16 16 - 16 15 - 16 12 - 14 19 - 20 15 - 17 17 - 18 17 - 18 18 - 18 12 - 12 15 - 16 16 - 18 16 - 18 10 - 12 12 15 - 15 8 - 10 18 6 - 14 18 - 18	7277557767777775135177

^a Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique.

 $^{^{\}rm b}$ N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value).

 $^{^{\}rm c}\,{\rm S}$ is the number of samples with results greater than the limit of quantitation.

d No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.



Standard Operating Procedures for Recycled Oil Sample Collection (#TPB 0017)

1.0 Purpose

The purpose of this SOP is to describe procedures to collect recycled oil samples from a variety of receptacles or containers (e.g. tank, drum, barrel, boiler, and etc.)

Note: For your personal safety, make sure that the facility operator collects recycled oil samples from the burner pipeline, large tanks and tank cars while the DAQ inspector observes the sample collection process and ensures that the DAQ recommended procedures be followed. It is considered that the inspectors are safe when collecting oil samples from drums, barrels, cans, etc. Again it is advised that you be the judge of the situation and your safety, which should be of prime importance.

2.0 References

The document "Recycled Oil Management Plan," December 2002 contains more details on recycled oil sample collection.

3.0 Equipment Description

Polyethylene Composite Liquid Waste Sampler (COLIWASA) recommended by the American Society for Testing and Materials (ASTM) shall be used as the recycled oil sample collection devise. The other equipment needs for this SOP are brown Nalgene bottles (capacity-1000ml), disposable hand gloves, waste container, tissue wipes, self-adhesive labels and shipping cases. *Use only disposable COLIWASA samplers. Once used throw them away and never re-use. Similarly, only new (unused) Nalgene bottles are to be used for* recycled *oil sample collection.*

4.0 Procedures

4.1 Calibration and Certification

4.2 General Procedures

Activities related to recycled oil sample collection are summarized in Table 4-1.

Table 4-1

Summary of Activities Related to Recycled Oil Collection	
Sample Activity	Program Plan
Equipment	Polyethylene Composite Liquid Waste Sampler (COLIWASA) and/or Drum Thief
Container	New 1000 ml Brown Nalgene Bottle
Volume	950 ml
Labeling and Identification	Use self-adhesive label and give sample number in the field and complete (write) the "Recycled Oil Sample Report."
Storage and Transportation	Samples are stored and shipped in closed containers. Transport samples to Toxics Lab within 3 working days. At the Toxics Lab, samples are aliquoted within 5 working days and sent to analytical labs.

- 4.2.1 Arrival at the Facility: The facility operator should be informed that a duplicate sample will be offered in a State-provided container and that after completion of sampling, he/she will be asked to sign "Recycled Oil Sample Report" acknowledging acceptance or rejection of a duplicate sample. The purpose of collecting a duplicate sample is to allow the facility the opportunity to analyze the same substance the State will be analyzing. While at the facility, obtain a copy of the analytical report of the recycled oil batch that will be sampled and attach it to the "Recycled Oil Sample Report." If this analytical report is not available, make arrangements for the Toxics Protection Branch to receive a copy by fax/mail.
- **4.2.2** <u>Sampling Equipment</u>: Use disposable COLIWASA for sample collection from barrels, drums, tanks, tank cars and a Drum Thief for small cans (for detail description of COLIWASA and Drum Thief, see Attachment 2 in "Recycled Oil Management Plan," December 2002).
- **4.2.3** Sample Container: Use a 1000 ml brown Nalgene bottle to collect recycled oil samples. Use only **new** brown colored bottles to prevent sample cross-contamination and to protect potential light-sensitive materials in the recycled oil samples. Do not fill more than 95% of the bottle capacity and leave room for thermal expansion of the sample during storage and transport.
- **4.2.4** <u>Sample volume</u>: Collect approximately 950 ml (95% capacity of a 1000 ml brown Nalgene bottle). There is no need for precise sample volume measurement. Analytical requirements are such that 950 ml sample volume is considered to be adequate.
- **4.2.5** <u>Sample Labeling and Identification</u>: It is imperative that the sample collected be immediately capped and labeled using "self-adhesive label" and should be additionally secured using clear tape. The person collecting

- the sample should record the sample number on the label in the field using the following format: example, Region/month/date/year/sample number ARO-030499-01-Asheville Region/March 04, 1999/sample number. For further details on sample labeling, refer to "Recycled Oil Management Plan," December 2002.
- 4.2.6 Recycled Oil Sample Report: This one is another important document and must be completed in the field by the person collecting sample, immediately after sample collection and labeling. A copy of the "Recycled Oil Sample Report" should be shipped along with samples to the Toxics Lab. For address and shipping details, refer to "Recycled Oil Management Plan," December 2002.
- 4.2.7 <u>Sample Storage and Transportation</u>: All samples, after collection and labeling, must be sealed with a chain-of custody (COC) seal and placed in the shipping container together with Recycled Oil Sample Report form and a Chain-of Custody form. Samples should be shipped within THREE working days after collection, to the Toxics Lab.
- 4.2.8 Recycled Oil Field Sample Collection: It is anticipated that most of the samples will be collected from facilities burning recycled oil in boilers, kilns, rotary dryers or furnaces. Such facilities may have recycled oil stored in tanks, tank cars, barrels, drums, cans, etc., Consequently, sample collection procedures detailed below only address these types of sources. Details related to any other sample collection procedure can be obtained by contacting the Toxics Protection Branch. The Sample collection procedures included below are those that are recommended by the ASTM:
 - Manual Burner Pipeline Sampling: This is the preferred method of recycled oil sampling since samples from this point source will represent the actual oil being combusted at the time of sample collection. Most burner fuel feed lines have a sample tap in the line from which an oil sample can be collected using the following steps:
 - a. Flush the sample tap and pipe until they are purged by allowing about 2000 ml of oil to pass through.
 - b. Collect the recycled oil sample into a 1000 ml brown Nalgene bottle, cap and label the bottle.

Caution: The fuel in these feed lines will be under pressure and may be heated. Therefore, take extreme care when opening the valve for sample collection.

- Storage Tank and Tank Cars: Storage tanks and tank cars generally hold large recycled oil volumes and these needs to be sampled as follows:
 - a. Insert an open disposable polyethylene COLIWASA, 7/8 inch in diameter and 7 feet long from the top of the tank to a depth of about 1 feet from the bottom.

- b. Pull up the plunger on COLIWASA and seal the end while removing the sample.
- c. Release the sample into Nalgene bottle.
- d. Repeat these steps until the desired sample volume of 950 ml is obtained.
- Drums, Barrels and Cans: Barrels, drums and cans containing recycled oil
 can be sampled using disposable COWLIWASA or Drum Thief. If there is
 more than one Barrel/drum at the facility, collect an equal volume portion
 from each to make up a composite sample volume of 950 ml. In this case,
 describe details of sampling and or sample locations in the "Recycled Oil
 Sample Report".

For drums and barrels, a 7/8 inch diameter and 42 inch long COLIWASA holding 250 ml sample volume is also ideal. Repeat all sample collection steps described in 4.8.2 to collect a 950 ml recycled oil sample.

Additionally, a Drum Thief (12-mm in diameter and 42 inches long) may be used to collect recycled oil samples:

- a. Insert the Drum Thief into the container, while covering the open end with your thumb.
- b. Remove the sampling device and transfer the sample into a 1000 ml Nalgene bottle.
- c. Repeat the above steps until the desired sample volume is obtained.

5.0 Maintenance

Not applicable

6.0 Safety

It is the policy of the Division of Air Quality (DAQ) that your personal safety is of prime importance during recycled oil sample collection. Ultimately, it is you that must determine in the field, whether or not sampling can be performed in a controlled and safe environment. For most sampling visits, Level D protective clothing is appropriate which should include use of steel-toed safety shoes or boots, hard hat, protective hand gloves, and safety glasses. For your personal safety, make sure that the facility operator collects recycled oil samples from the burner pipeline, large tanks and tank cars while the DAQ inspector observes the sample collection process and ensures that the DAQ recommended procedures be followed. It is considered that the inspectors are safe when collecting oil samples from drums, barrels, cans, etc. Again it is advised that you be the judge of the situation and your safety, which should be of prime importance. Always take a waste container for disposal of wipes and gloves and dispose these items in appropriate waste containers, preferably on the facility property.

7.0 General Notes and Comments

Not applicable

8.0 Storage

There are no specific storage requirements for recycled oil samples. Samples are reported to be stable at room temperature for at least 6 (six) months.

9.0 Attachments

For additional details refer to "Recycled Oil Management Plan," December 2002.

RECYCLED OIL ALIQUOTING

1.0 Purpose

The purpose of this document is to define a standard operating procedure (SOP) for the recycled oil sample aliquoting.

2.0 References

North Carolina Division of Air Quality "Recycled Oil Management Plan"

3.0 Equipment Description

Amber Nalgene Sample bottle 500 ml, funnel, safety glasses, Gloves, fume hood.

4.0 Procedures

4.1 The samples received in the laboratory must be in a 1000 ml amber Nalgene sample bottles.

4.2 General Operations

Under a hood the 1000 ml sample should be agitated properly to maintain a homogeneous sample. The sample is poured using a funnel into two 500 ml bottles.

5 Maintenance

The funnel should be washed in hot water and detergent after every use. Use new Nalgene sample bottles for every recycled oil sample.

6 Safety

All sample aliquoting should be done under a hood. Gloves and aprons and safety glasses will be used at all times.